

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
14 February 2002 (14.02.2002)

PCT

(10) International Publication Number
WO 02/12403 A2

(51) International Patent Classification⁷: C09B 69/10,
C09D 133/04, C08F 220/38, 290/14

(21) International Application Number: PCT/US01/24640

(22) International Filing Date: 6 August 2001 (06.08.2001)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
60/223,520 7 August 2000 (07.08.2000) US
09/920,151 1 August 2001 (01.08.2001) US

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(81) Designated States (*national*): CA, JP, MX.

(84) Designated States (*regional*): European patent (AT, BE,
CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC,
NL, PT, SE, TR).

Published:

— without international search report and to be republished
upon receipt of that report

*For two-letter codes and other abbreviations, refer to the "Guid-
ance Notes on Codes and Abbreviations" appearing at the begin-
ning of each regular issue of the PCT Gazette.*

(54) Title: COLORANTS CONTAINING COPOLYMERIZABLE VINYL GROUPS AND SULFONAMIDE LINKAGES

(57) Abstract: Disclosed are thermally-stable, colored, photopolymerizable compounds containing a vinyl group which are capable of being copolymerized with reactive vinyl monomers to produce colored compositions such as polyacrylates, polymethacrylates, polystyrene, etc. The compounds exhibit good thermal stability, fastness (stability) to UV-light, good solubility in the reactive monomers and good color strength.

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COLORANTS CONTAINING COPOLYMERIZABLE
VINYL GROUPS AND SULFONAMIDE LINKAGES

Cross Reference to Related Application

5 This application claims the benefit of United States Provisional Application
Serial No. 60/223,520 filed August 07, 2000.

Field of the Invention

10 This invention pertains to thermally-stable, colored, photopolymerizable
compounds containing a vinyl group which are capable of being copolymerized
with reactive vinyl monomers to produce colored compositions such as
polyacrylates, polymethacrylates, polystyrene, etc. The compounds exhibit good
thermal stability, fastness (stability) to UV-light, good solubility in the reactive
monomers and good color strength.

15

Background and Prior Art

 It is known (J.S.D.C., April 1977, pp 114-125) to produce colored
polymeric materials by combining a reactive polymer such terepolymers having
epoxy groups or polyacryloyl chloride with anthraquinone dyes containing
20 nucleophilic reactive groups such as amino or hydroxy groups; to graft
acryloylaminoanthraquinone dyes to the backbone of vinyl or divinyl polymers;
and to polymerize anthraquinone dyes containing certain olefinic groups to produce
polymeric dyes/pigments. U.S. Patent 4,115,056 describes the preparation of blue,
substituted 1,4-diaminoanthraquinone dyes containing one acryloyloxy group and
25 and the use of the dyes in coloring various fibers, especially polyamide fibers. U.S.
Patent 4,943,617 discloses liquid crystalline copolymers containing certain blue,
substituted 1,5-diamino-4,8-dihydroxyanthraquinone dyes containing an olefinic
group copolymerized therein to provide liquid crystal copolymers having high
dichromism. U.S. Patent 5,055,602 describes the preparation of certain substituted
30 1,4-diaminoanthraquinone dyes containing polymerizable acryloyl and

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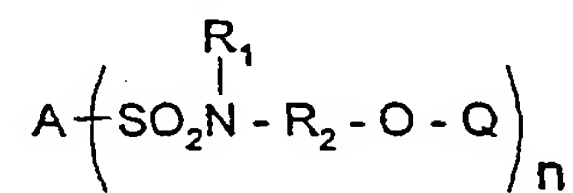
methacryloyl groups and their use in coloring polyacrylate contact lens materials by copolymerizing.

U.S. Patent 5,362,812 discloses the conversion of a variety of dye classes, including anthraquinones, into polymeric dyes by (a) polymerizing
 5 2-alkenylazlactones and reacting the polymer with dyes containing nucleophilic groups and by (b) reacting a nucleophilic dye with an alkenylazlactone and then polymerizing the free radically polymerizable dyes thus produced. The polymeric dyes are reported to be useful for photoresist systems and for colorproofing. U.S. Patent 5,367,039 discloses a process for preparing colored vinyl polymers suitable
 10 for inks, paints, toners and the like by emulsion polymerization of a vinyl monomer with reactive anthraquinone dyes prepared by functionalizing certain anthraquinone dyes with methacryloyl groups.

The preparation of a variety of dyes, including some anthraquinones, which contain photopolymerizable groups and their use for color filters suitable for use in
 15 liquid crystal television sets, color copying machines, photosensitive resist resin compositions, and the like are described in U.S. Patent 5,578,419.

Brief Summary of the Invention

One embodiment of the present invention concerns thermally-stable,
 20 photopolymerizable dye or colorant compounds having having Formula I:



I

wherein

A is a mono-, di-, tri- or tetravalent chromophore;
 25 R₁ is selected from hydrogen, C₁ - C₆ alkyl, substituted C₁ - C₆ alkyl, C₃ - C₈ cycloalkyl, aryl and -R₂-OQ;

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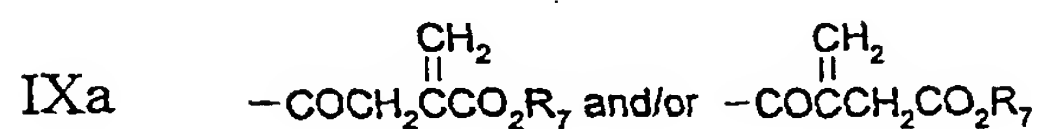
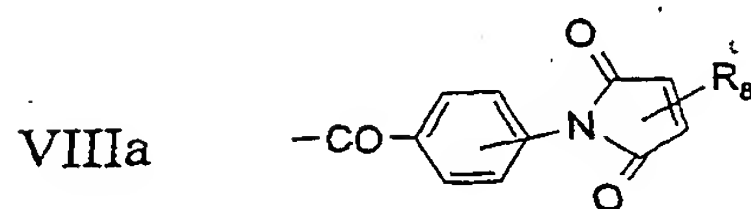
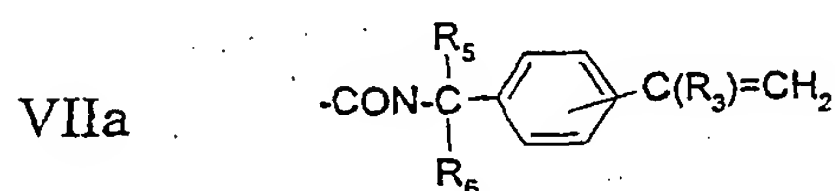
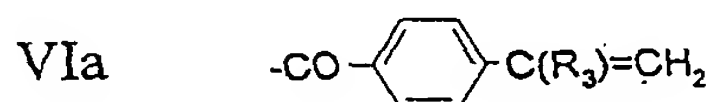
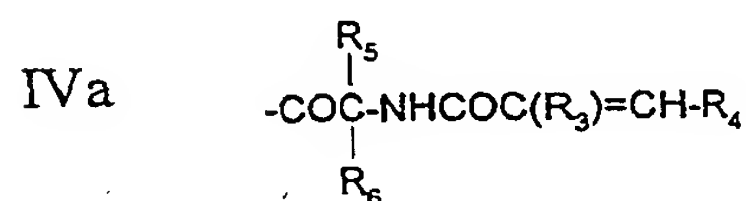
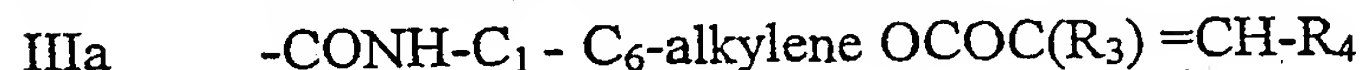
R_2 is selected from $C_2 - C_8$ alkylene, arylene, $C_3 - C_8$ cycloalkylene, arylene - $C_1 - C_6$ alkylene, arylene-oxy- $C_1 - C_6$ alkylene, arylene-thio - $C_1 - C_6$ alkylene, 1,4-cyclohexylenedimethylene and $(-CH_2CH_2O)_m-CH_2CH_2-$;

m is 1-3;

5

n is 1-4;

Q is an ethylenically-unsaturated, photopolymerizable group selected from the following organic radicals:



wherein

10

R_3 is selected from hydrogen or $C_1 - C_6$ alkyl;

R_4 is selected from hydrogen, $C_1 - C_6$ alkyl;

phenyl; phenyl substituted with one or more groups selected from $C_1 - C_6$ alkyl,

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5 C₁ - C₆ alkoxy, -N(C₁ - C₆ alkyl)₂, nitro, cyano, C₂ - C₆ alkoxy carbonyl, C₂ - C₆ alkanoyloxy and halogen; 1- and 2-naphthyl; 1- and 2-naphthyl substituted with C₁ - C₆ alkyl and C₁ - C₆ alkoxy; 2- and 3-thienyl; 2- and 3-thienyl substituted with C₁ - C₆ alkyl or halogen; 2- and 3-furyl; 2- and 3-furyl substituted with C₁ - C₆ alkyl;

R₅ and R₆ are independently selected from hydrogen, C₁ - C₆ alkyl, substituted C₁ - C₆ alkyl, aryl or may be combined to represent a $-(\text{-CH}_2\text{-})_{3-5}$ radical;

10 R₇ is hydrogen or a group selected from C₁ - C₆ alkyl, substituted C₁ - C₆ alkyl, C₃ - C₈ alkenyl, C₃ - C₈ cycloalkyl and aryl;

R₈ is selected from hydrogen, C₁ - C₆ alkyl and aryl.

A second embodiment of the present invention pertains to a coating composition comprising (i) one or more polymerizable vinyl compounds, (ii) one or more of the thermally-stable, photopolymerizable dye or colorant compounds of Formula I, and (iii) a photoinitiator. A third embodiment of the present invention pertains to a polymeric composition, typically a coating, comprising a polymer of one or more acrylic acid esters, one or more methacrylic acid esters and/or other polymerizable vinyl compounds, having copolymerized therein one or more of the dye compounds of Formula I.

20

Detailed Description of the Invention

In formula I, A represents a mono-, di-, tri- or tetravalent residue of a chromophore, i.e., a colored compound. Examples of the chromophoric residues which A may represent include anthraquinone, anthrapyridone (3H-dibenz-[f, ij]-isoquinoline-2,7-dione), anthrapyrimidine (7H-benzo-[e]-perimidine-7-one), anthrapyridine (7H-dibenz-[f, ij]-isoquinoline-7-one), anthrapyrazole, anthraiso-thiazole, 14H-naptho[2,3-a]-phenothiazine-8,13-dione (phthaloylphenothiazine), phthalocyanine, metal phthalocyanine, methine, bis-methine, perinone, coumarin, quinophthalone, 3-aryl-2,5-dioxypyrroline, and 3-aryl-5-dicyanomethylene-2-oxypyrroline.

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- 5 -

The terms "C₁ - C₆-alkyl" and "C₁ - C₈-alkyl" are used herein to denote a straight or branched chain saturated aliphatic hydrocarbon radical containing one to six or one to eight carbon atoms. The term "substituted C₁ - C₆-alkyl" is used to denote a C₁ - C₆-alkyl group substituted with one or more groups, preferably one to three groups, selected from the group consisting of hydroxy, halogen, cyano, aryl, aryloxy, arylthio, C₁ - C₆ alkylthio, C₃ - C₈-cycloalkyl, C₂ - C₆-alkanoyloxy and $-(OR_9)_p-R_{10}$ wherein R₉ is selected from the group consisting of C₁ - C₆ alkylene, C₁ - C₆-alkylene-arylene, cyclohexylene, arylene, C₁ - C₆-alkylene-cyclohexylene and C₁ - C₆-alkylene-cyclohexylene-C₁ - C₆-alkylene; R₁₀ is selected from the group consisting of hydrogen, hydroxy, carboxy, C₂ - C₆-alkanoyloxy, C₂ - C₆-alkoxy-carbonyl, aryl and C₃ - C₈-cycloalkyl; and p is 1, 2, or 3.

The terms "C₁ - C₆-alkylene", "C₂ - C₆-alkylene" and "C₂ - C₈ alkylene" are used to denote straight or branched chain divalent aliphatic hydrocarbon radicals containing one to six, two to six, and two to eight carbons, respectively, which optionally may be substituted with one to three groups selected from C₁ - C₆-alkoxy, C₂ - C₆-alkoxycarbonyl, C₂ - C₆-alkanoyloxy, hydroxy, aryl and halogen. The term "C₃ - C₈-alkenyl" is used to denote an aliphatic hydrocarbon radical containing at least one double bond. The term "C₃-C₈-alkynyl" is used to denote an aliphatic hydrocarbon radical containing at least one triple bond and three to eight carbon atoms. The term "C₃ - C₈-cycloalkyl" is used to denote a saturated cyclic hydrocarbon radical having three to eight carbon optionally substituted with one to three C₁ - C₆-alkyl group(s). The term "C₃ - C₈-cycloalkylene" is used to denote a cyclic divalent hydrocarbon radical which contains three to eight carbon atoms, preferably five or six carbons.

The term "aryl" as used herein denotes phenyl and phenyl substituted with one to three substituents selected from C₁ - C₆-alkyl, substituted C₁ - C₆-alkyl, C₁ - C₆-alkoxy, halogen, carboxy, cyano, C₂ - C₆-alkanoyloxy, C₁ - C₆-alkylthio, C₁ - C₆-alkylsulfonyl, trifluoromethyl, hydroxy, optionally substituted sulfamoyl, C₂ - C₆-alkoxycarbonyl, C₂ - C₆-alkanoylamino and -O-R₁₁, S-R₁₁, -SO₂-R₁₁, -NHSO₂R₁₁ and -NHCO₂R₁₁, wherein R₁₁ is phenyl or phenyl substituted with one to three

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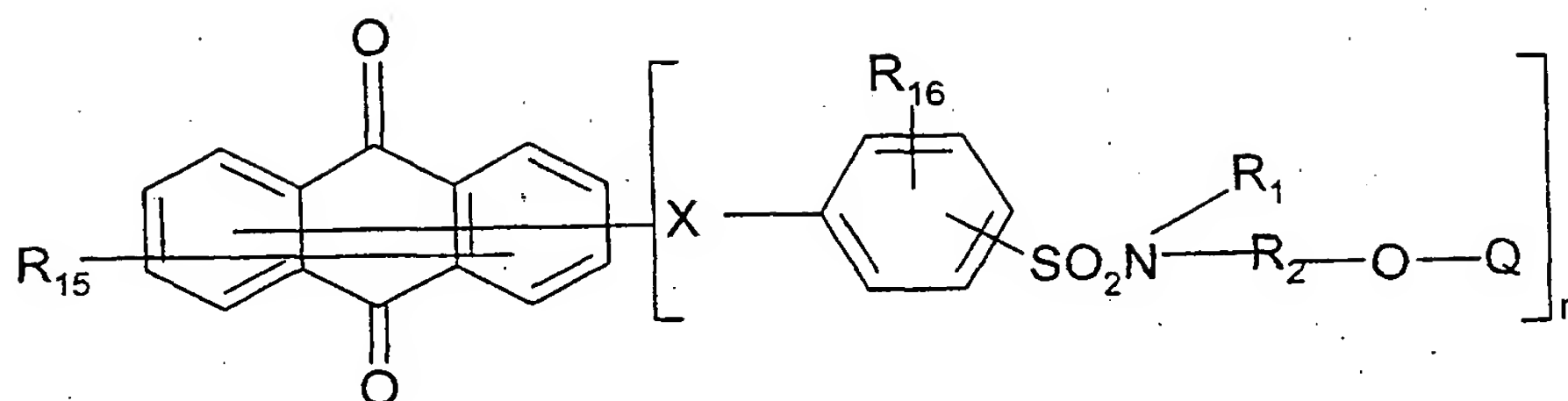
groups selected from C₁ - C₆-alkyl, C₁ - C₆-alkoxy and halogen. The term "arylene" as used herein denotes includes 1,2-, 1,3- and 1,4-phenylene and such divalent radicals substituted with one to three groups selected from C₁ - C₆-alkyl, C₁ - C₆-alkoxy and halogen. The term "aaryl" denotes a moiety having the formula
5 -CO-R₁₁ wherein R₁₁ is defined above.

The term "halogen" is used to include fluorine, chlorine, bromine, and iodine. The term "optionally substituted sulfamoyl" is used to describe the group having the structure -SO₂N(R₁₂)R₁₃, wherein R₁₂ and R₁₃ are independently selected from hydrogen, C₁ - C₆-alkyl, substituted C₁ - C₆-alkyl, C₃ - C₈-alkenyl, C₃
10 - C₈-cycloalkyl, aryl and heteroaryl. The terms "C₁ - C₆-alkoxy", "C₂ - C₆-alkoxycarbonyl", "C₂ - C₆-alkanoyl", "C₂ - C₆-alkanoyloxy" and "C₂ - C₆-alkanoylamino" are used to denote radicals corresponding to the structures -OR₁₄, -COR₁₄, -CO₂ R₁₄, -OCOR₁₄ and NHCOR₁₄, respectively, wherein R₁₄ is C₁ - C₆-alkyl or substituted C₁ - C₆-alkyl.

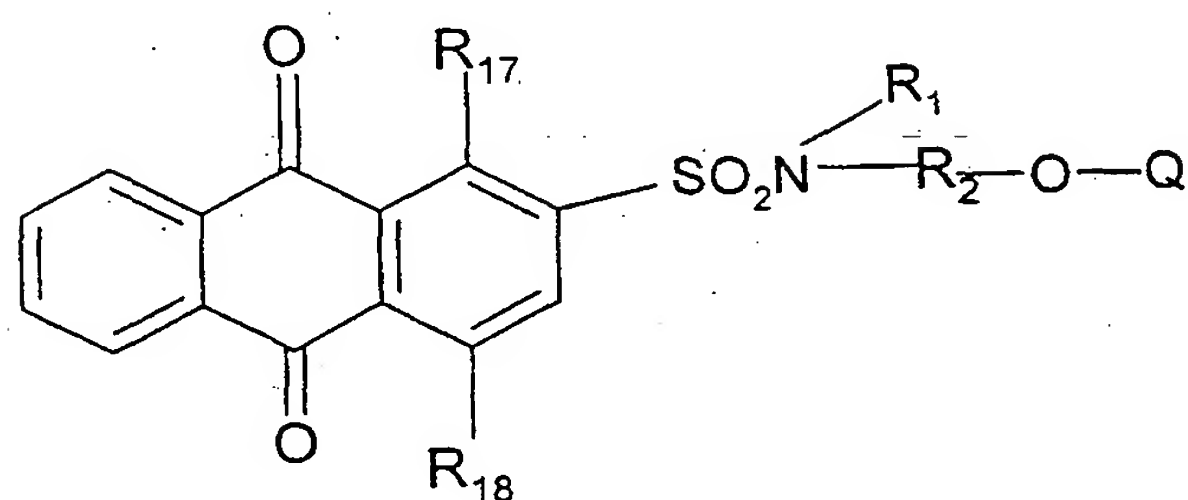
15 The term "heteroaryl" as used herein denotes a 5- or 6- membered aromatic ring containing one to three hetero atom selected from oxygen, sulfur and nitrogen. Examples of such heteroaryl groups are thienyl, furyl, pyrrolyl, imidazolyl, pyrazolyl, thiazolyl, isothiazolyl, oxazolyl, isoxazolyl, triazolyl, thiadiazolyl, oxadiazolyl, tetrazolyl, pyridyl, pyrimidyl, benzoxazolyl, benothiazolyl,
20 benzimidazolyl, indolyl and the like and these optionally substituted with one to three groups selected from C₁ - C₆-alkyl, C₁ - C₆-alkoxy, substituted C₁ - C₆-alkyl, halogen, C₁ - C₆-alkylthio, aryl, arylthio, aryloxy, C₂ - C₆-alkoxycarbonyl and C₂ - C₆-alkanoylamino.

25 The preferred anthraquinone dyes or colorants of the invention which correspond to Formula I have the following structures:

- 7 -

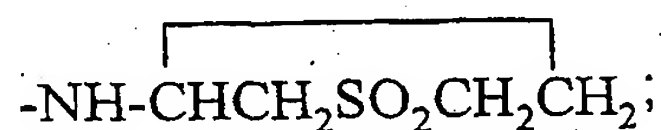


X



XI

- wherein R_{15} is hydrogen or R_{15} represents 1-4 groups selected from amino; C_1 - C_8 -alkylamino; C_1 - C_8 -alkylamino substituted with one or more groups selected from hydroxy, cyano, halogen, aryl, heteroaryl, C_3 - C_8 -cycloalkyl, furyl, C_1 - C_6 -alkoxy, C_1 - C_6 -alkylthio, arylthio, aryloxy and $-OCH_2CH_2O(OCH_2CH_2)_{1-3}OR'$, wherein R' is selected from hydrogen, C_1 - C_6 -alkyl and C_2 - C_6 -alkanoyloxy; C_3 - C_8 -cycloalkyl-amino; C_3 - C_8 -alkenylamino; C_3 - C_8 -alkynylamino; arylamino; furfurylamino; C_1 - C_6 -alkoxy; $-OCH_2CH_2(OCH_2CH_2)_{1-3}OR'$, wherein R' is as previously defined; halogen; hydroxy; C_1 - C_6 -alkylthio; arylthio; aryl; aryloxy; arylsulfonyl; C_2 - C_6 -alkanoyl; aroyl; C_2 - C_6 -alkanoyloxy; C_2 - C_6 -alkoxycarbonyl; heteroaryl; heteroarylthio; cyano; nitro; trifluoromethyl; thiocyno; $-SO_2C_1$ - C_6 -alkyl; $-SO_2NH_2$; $-SO_2NHC_1$ - C_6 -alkyl; $-SO_2N(C_1$ - C_6 alkyl) $_2$; $-SO_2N(C_1$ - C_6 alkyl)aryl; $-SO_2NH$ -aryl; $-CONH_2$; $-CONHC_1$ - C_6 -alkyl; $-CON(C_1$ - C_6 -alkyl) $_2$; $-CONH$ -aryl; $-CON(C_1$ - C_6 alkyl) aryl; C_1 - C_6 alkyl; tetrahydrofurfurylamino; $-CH_2$ -cyclohexane-1,4-diyl- CH_2OR' , wherein R' is as previously defined; or



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R_{16} is hydrogen or 1-2 groups selected from C_1 - C_6 -alkyl, C_1 - C_6 -alkoxy and halogen;

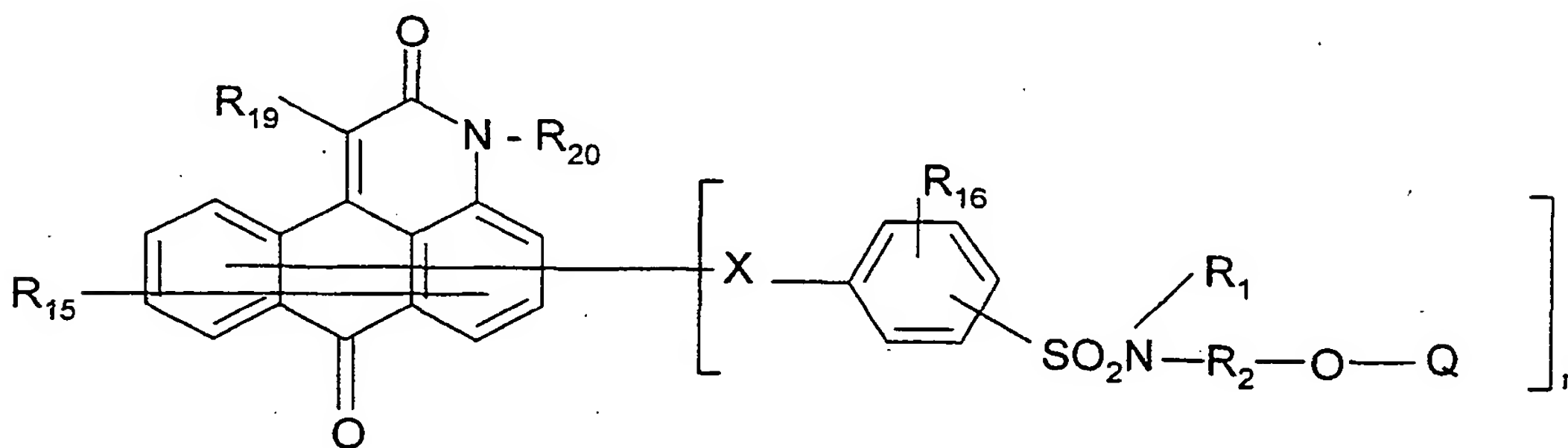
R_{17} is selected from amino; C_1 - C_8 -alkylamino, substituted C_1 - C_8 -alkylamino is defined above, C_3 - C_8 -cycloalkylamino, C_3 - C_8 -alkenylamino, C_3 - C_8 -alkynylamino and arylamino;

R_{18} is selected from halogen, amino, C_1 - C_8 alkylamino, substituted C_1 - C_8 -alkylamino, C_3 - C_8 -cycloalkylamino, C_3 - C_8 -alkenylamino, C_3 - C_8 -alkynylamino, arylamino, hydroxy, arylthio, heteroarylthio, C_2 - C_6 -alkanoylamino, aroylamino, C_1 - C_6 -alkylsulfonylamino, and arylsulfonylamino;

X is a covalent bond or a linking group selected from $-O-$, $-S-$, $-SO_2-$, $-NHCO-$, $-NHCO_2-$, $-NHCONH-$, $-OC_2-C_6$ alkylene-, $-OC_2-C_6$ -alkylene- $O-$, $-S-C_2-C_6$ -alkylene- $O-$ and, $-O(CH_2CH_2O)_{1-3}-$; and

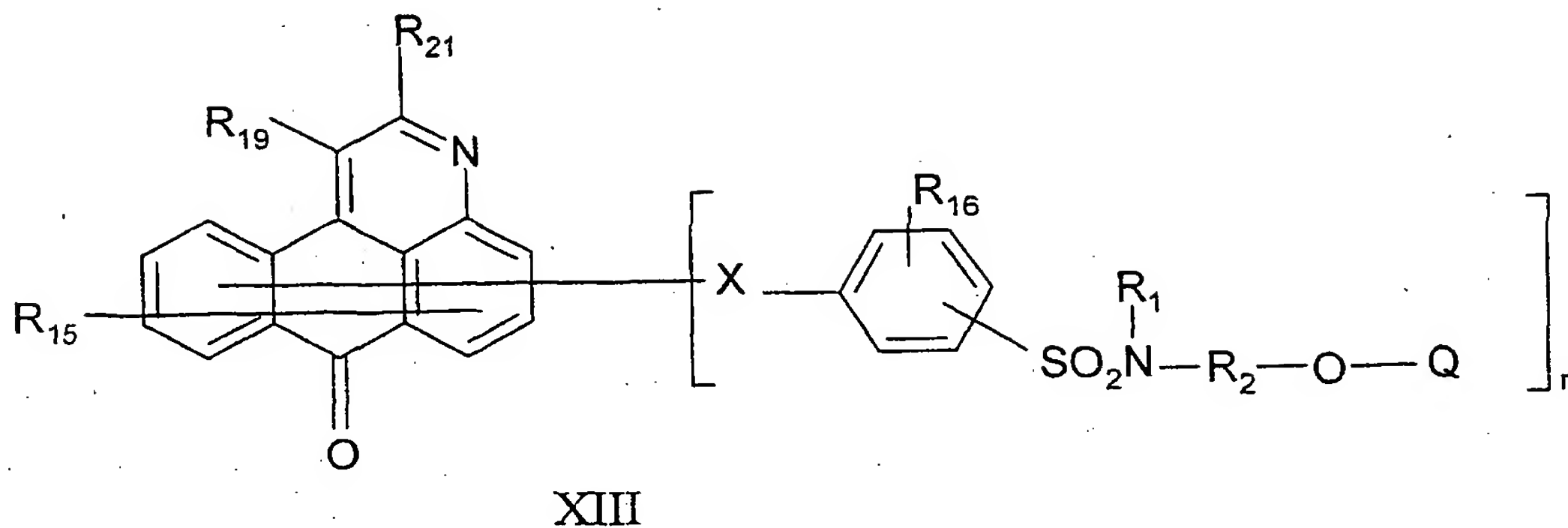
R_1 , R_2 , Q and n are as defined above for Formula I.

Preferred anthrapyridone (3H-dibenz[f, ij]-isoquinoline-2,7-diones) and anthrapyridine (7H-dibenz-[f, ij]-isoquinoline-7-ones) colorant compounds provided by the present invention have the following general formulas:



XII

- 9 -



wherein:

5 R_{19} is selected from hydrogen, cyano, C_1 - C_6 -alkoxy, C_1 - C_6 -alkylthio, aryl, arylamino, aryloxy, arylthio, heteroaryl, heteroarylthio, halogen, C_2 - C_6 -alkoxy-carbonyl, aroyl, C_1 - C_6 -alkylsulfonyl, arylsulfonyl and C_1 - C_6 -alkylamino;

R_{20} is selected from hydrogen, C_1 - C_8 -alkyl, substituted C_1 - C_8 -alkyl as defined above, aryl and C_3 - C_8 -cycloalkyl;

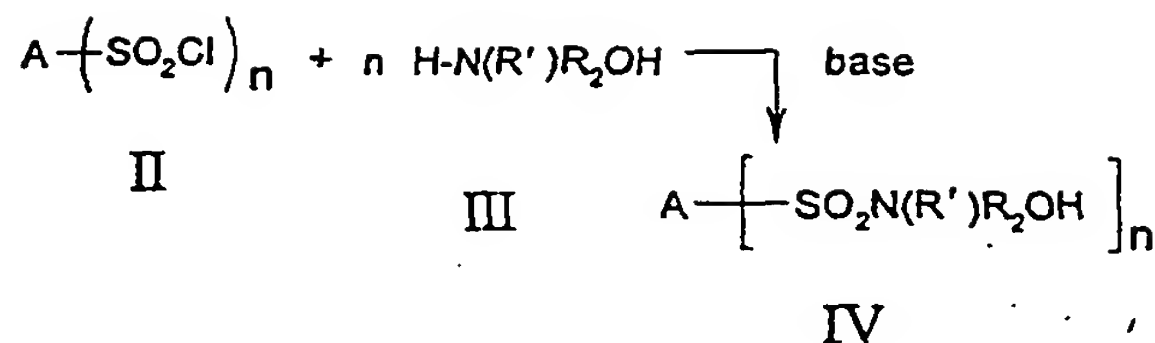
10 R_{21} is selected from hydrogen, C_1 - C_6 -alkyl, aryl and $-N(R_{22})R_{23}$, wherein R_{22} and R_{23} are independently selected from hydrogen, C_3 - C_8 -cycloalkyl, C_1 - C_6 -alkyl and C_1 - C_6 -alkyl substituted with C_1 - C_6 -alkoxy, hydroxy, halogen, C_2 - C_6 -alkanoyloxy, aryl and C_3 - C_8 -cycloalkyl; wherein R_{22} and R_{23} also may be combined to produce divalent radicals such as $(-CH_2-)_{4-6}$ and $-CH_2CH_2-L-CH_2CH_2-$, wherein L is a divalent linking group selected from $-O-$, $-S-$, $-SO_2-$ and $-N(R_{24})$, wherein R_{24} is selected from hydrogen, C_1 - C_6 -alkyl, aryl, aroyl, C_2 - C_6 -akanoyl, C_1 - C_6 -alkylsulfonyl and arylsulfonyl; and

15 R_1 , R_2 , R_{15} , R_{16} , $-X-$, Q and n are defined above.

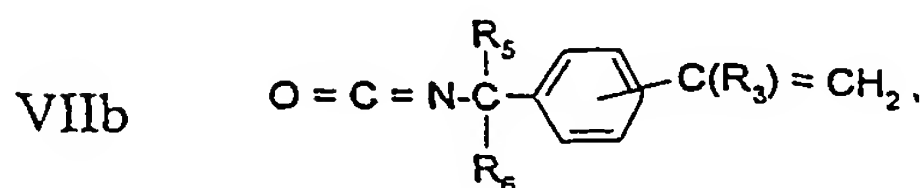
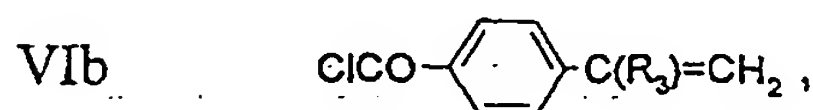
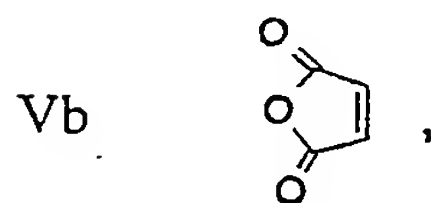
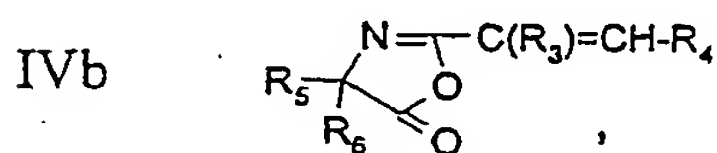
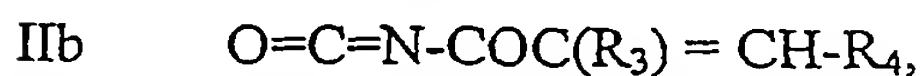
The thermally stable photopolymerizable colorants of Formula I may be prepared by reacting sulfonyl chlorides of Formula II with amines of Formula III,

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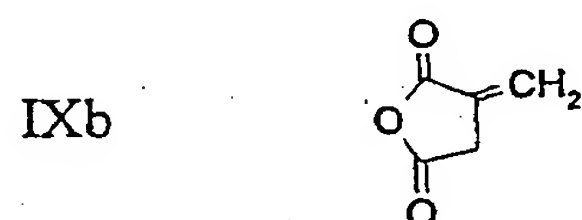
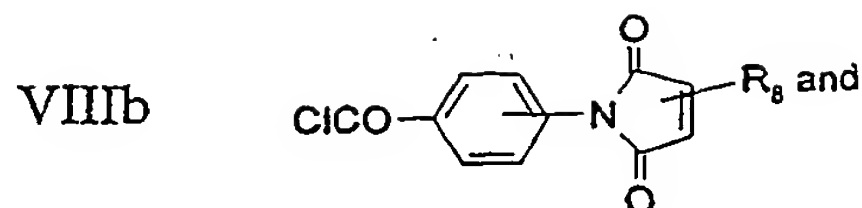
- 10 -



wherein R' is selected from hydrogen, C₁ - C₆ alkyl, substituted C₁ - C₆ alkyl, C₃ - C₈ - cycloalkyl, aryl and -R₂OH, in the presence of base or enough excess amine reactant III to serve as acid acceptor. Typical useful bases are alkali metal carbonates, alkali metal bicarbonates, trialkylamines, etc. The reactions may be carried out in excess amine reactant HN(R')R₂OH or in solvents such as ketones, pyridine, N,N-dimethylformamide (DMF), N-methyl-2-pyrrolidinone (NMP), N,N-dimethylacetamide (DMAC), sulfolane, etc. The colored intermediate hydroxy compounds IV thus produced are then acylated with one or more ethylenically-unsaturated, acylating agent to yield the colorants of Formula I. Examples of the ethylenically-unsaturated acylating agents include compounds having the formulas:



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Examples of intermediate sulfonyl chlorides II useful in the practice of the invention are described in U.S. Patents 4,403,092; 5,372,864; 5,453,482; 6,022,944 and Published PCT Application WO 98/23690. Additional sulfonyl chlorides of formula II are known and/or can be prepared according to published procedures.

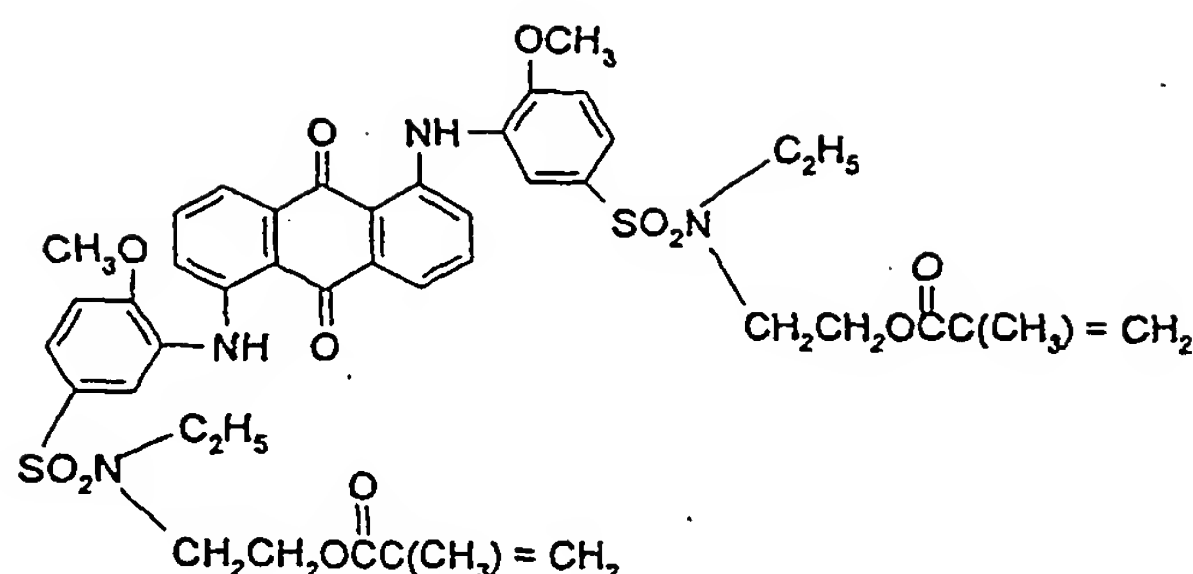
Colorant Examples

The thermally-stable, colored, photopolymerizable compounds containing a vinyl group provided by the present invention and the preparation thereof are further illustrated by the following examples:

EXAMPLE 1

A mixture of 1,5-bis-[5-(N-ethyl-N-(2-hydroxyethyl)sulfamoyl)-2-methoxyanilino]anthraquinone (U.S. Patent 5,372,864, Example 21) (2.0g, 2.66 mmol) and toluene (10 mL) was stirred and most of the toluene was removed under reduced pressure. DMF (50 mL), 4-(dimethylamino)pyridine (DMAP) (65mg), triethylamine (1.1 mL), hydroquinone (20mg) and methacrylic anhydride (1.22g, 7.98 mmol) were added and the reaction mixture was stirred overnight at room temperature for about 15 hours. The functionalized blue dye was precipitated by drowning into water (200 mL) and allowing the mixture to stand for several days at room temperature and was collected by filtration washed with water and dried in vacuo. Essentially a quantitative yield was obtained. FDMS supported the following structure:

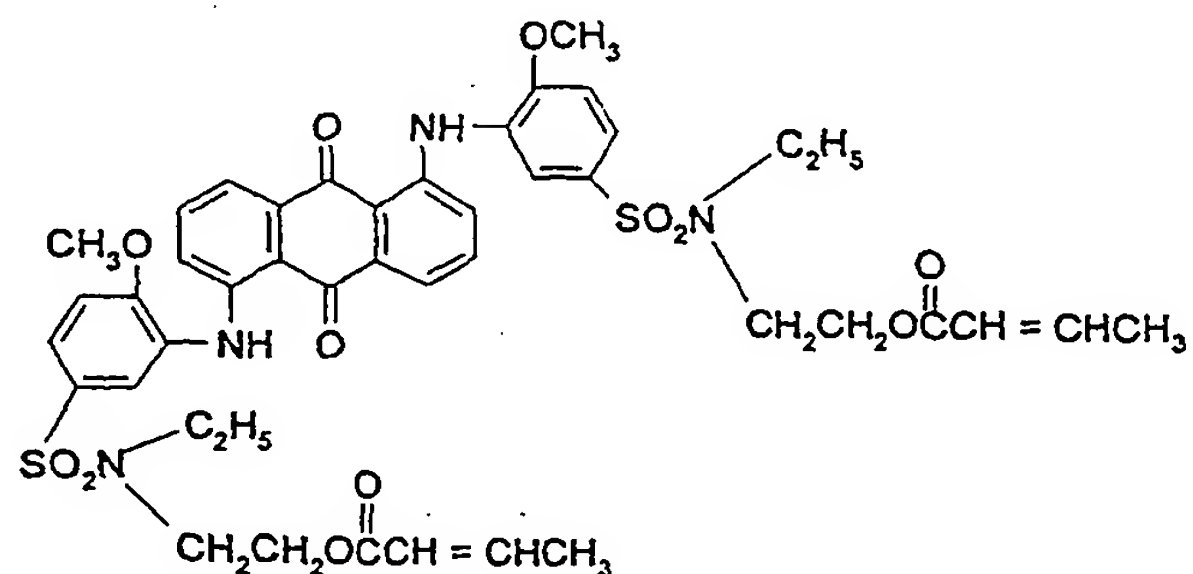
- 12 -



An absorption maximum at 527nm in DMF solution was observed in the UV-visible absorption spectrum.

5 EXAMPLE 2

A mixture of 1,5-bis-[5-(N-ethyl-N-(2-hydroxyethyl) sulfamoyl)-2-methoxyanilino]-anthraquinone (U.S. Patent 5,372,864, Example 21) (2.0g, 2.66 mmol) and toluene (10 mL) were stirred and most of the toluene removed under reduced pressure. DMF (50 mL), DMAP (65mg), triethylamine (1.1 mL), hydroquinone (20mg) and crotonic anhydride (1.23g, 7.98 mmol) were added. After being stirred at room temperature for 24 hours the reaction mixture was drowned into water (200 mL) and the mixture allowed to stand for awhile. The functionalized red dye was collected by filtration, washed with water and dried in vacuo. The yield was 1.96g of product (83% of the theoretical yield). FDMS supported the following structure:



An absorption maximum at 529nm was observed in the UV-visible light absorption spectrum.

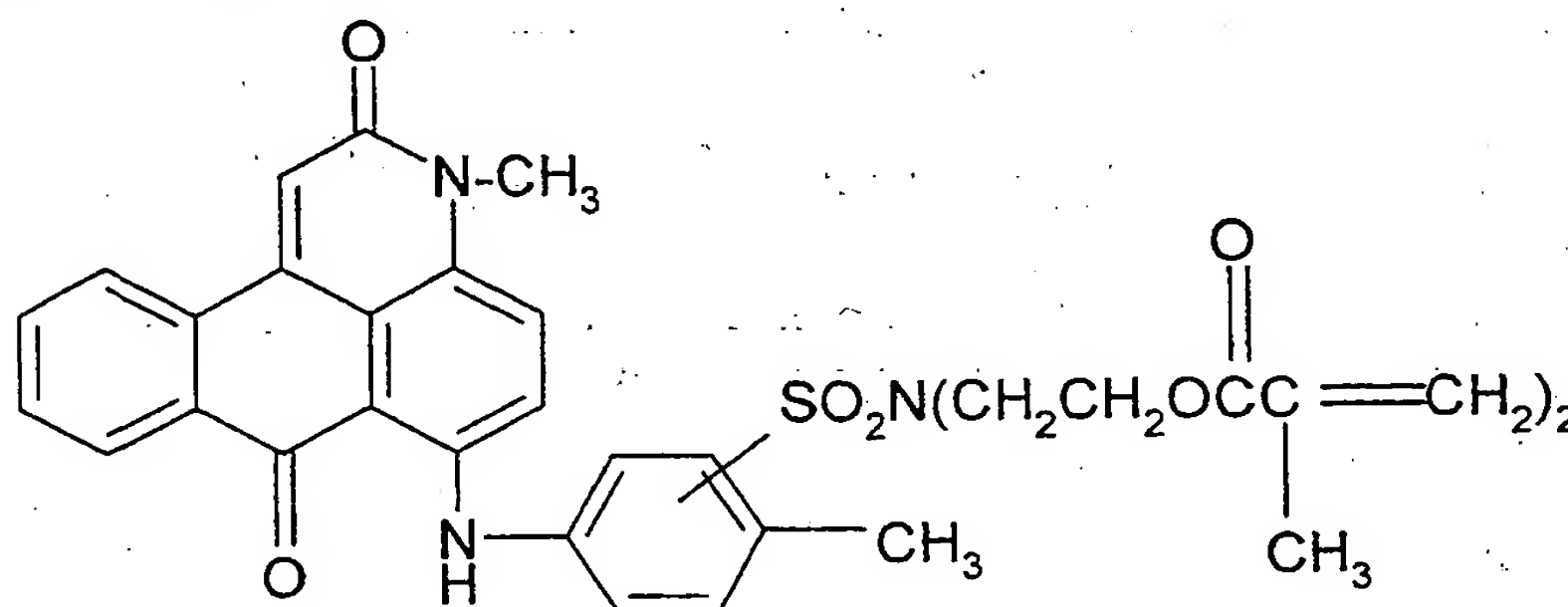
- 13 -

EXAMPLE 3a

To chlorosulfonic acid (10.0 ml) was added portionwise with stirring 3-methyl-6-(p-toluidino)-3H-dibenz-[f, ij]-isoquinoline-2,7-dione (2.0g, .00546m) allowing the temperature to rise. The reaction mixture was stirred for 1.0 hour with
5 no cooling or heating and then gradually poured into 50 ml of saturated sodium chloride solution with ice added for cooling. The red sulfonyl chloride product was collected by filtration, washed with water and then added to diethanolamine (25 ml). The reaction mixture was stirred occasionally and heated at 95-100°C for 30 minutes. The reaction mixture was drowned into 100 ml of water plus 50 ml of
10 saturated sodium chloride solution and the resulting mixture was heated to about 80°C and then filtered by vacuum filtration. After being washed with water the red product was dried in air (yield – 2.4g, 80% of the theoretical yield).

EXAMPLE 3b

15 A portion of the sulfonamide product from Example 3a (1.0g, 0.00187m), N,N-dimethylformamide (DMF)(25ml), hydroquinone (10mg) and 4-dimethylaminopyridine (DMAP)(46 mg) were mixed together and the reaction mixture was stirred while methacrylic anhydride (0.838 ml) was added followed by the dropwise addition of triethylamine (0.785 ml). After being stirred at room
20 temperature for 24 hours, the reaction mixture was drowned into water (50 ml). The dark red product was collected by filtration, washed with water and dried in air (yield 1.0g), 80% of the theoretical yield). FDMS supports the following structure:



- 14 -

An absorption maximum was observed at 534 nm in the UV-visible absorption spectrum.

EXAMPLE 4a

5 To chlorosulfonic acid (95.0g) was added 1-amino-2-bromo-4-(o-anisidino) anthraquinone (12.69g), 0.03 mol) portionwise with stirring, at 25-29°C, over about 1.25 hours. After being heated at about 75°C for 0.5 hour, the reaction mixture was drowned into isopropanol (1.0L) with stirring and using an ice bath for cooling. After being stirred for 15 minutes, the drowning mixture was filtered by vacuum
10 and the collected solid was washed with isopropanol and dried in a vacuum oven at room temperature (yield – 12.01g, 77% of the theoretical yield).

EXAMPLE 4b

 A portion of the 1-amino-2-bromo-4-(5'-chlorosulfonyl-2'-methoxy)anilino-
15 anthraquinone from Example 4a (5.21g, 0.01 mol) was mixed and stirred with tetrahydrofuran (THF) (125ml). To this stirred mixture was added a solution of diethanolamine (3.18g, 0.03m) which was dissolved in THF. After stirring the reaction mixture for 50 minutes at room temperature, the THF was removed by using a vacuum rotary evaporator. The product was dissolved in 2-ethoxyethanol
20 (175 ml) and this solution was then drowned into cold water (800 ml) to yield the solid blue product, which was collected by filtration, reslurried in hot water, filtered, washed with hot water and dried in air (yield – 3.66 g, 62% of the theoretical yield). FDMS showed the structure to be 1-amino-2-bromo-4[5'-(N,N-bis-2-hydroxyethyl)-sulfamoyl]-2'-methoxyanilino]anthraquinone.

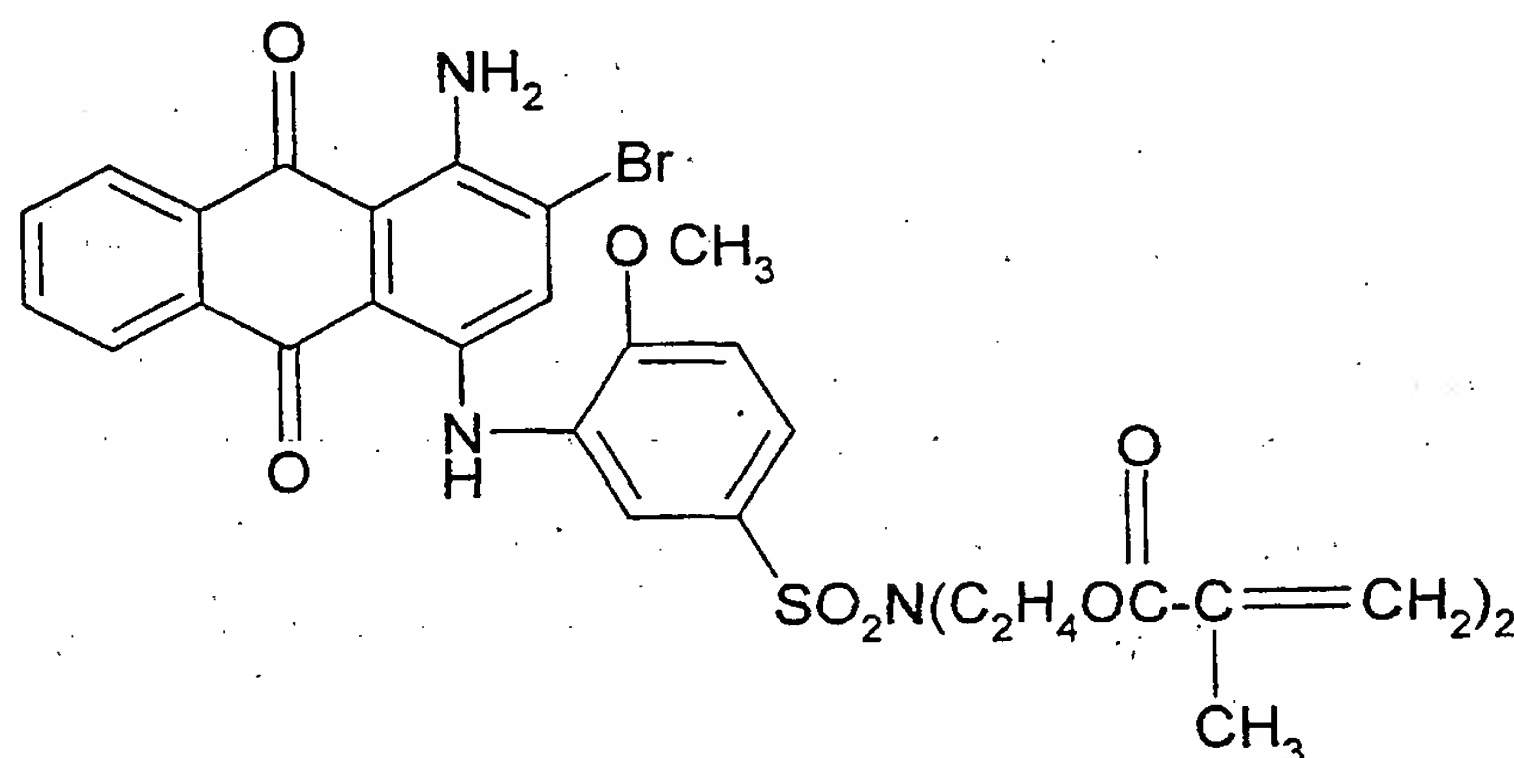
25

EXAMPLE 4c

 A portion (1.0g, 0.00169 mol) of the product from Example 4b, DMF (25.0 ml), hydroquinone (10mg) and DMAP (41 mg) were mixed and stirred while methacrylic anhydride (0.757 ml) was added followed by the dropwise addition of
30 triethylamine (0.708 ml). The reaction mixture was stirred at ambient temperature

- 15 -

for 24 hours and then drowned into water (50 ml). The solid product was collected by filtration, washed with water and dried in air (yield – 1.23 g, 84% of the theoretical yield). FDMS supported the following structure:



5

An absorption maximum was observed at 587 nm in the UV-Visible absorption spectrum in DMF as solvent.

EXAMPLE 5a

10 To chlorosulfonic acid (95 ml) was added portionwise 1,4-bis-(2',4'-dimethylanilino)anthraquinone (13.38g, 0.03 mol) with stirring at 25 - 28°C. The reaction mixture was stirred at room temperature for 1.5 hours, heated for 30 minutes at 65 - 70°C and then heated at about 95°C for 40 minutes. After being cooled to room temperature, the reaction mixture was drowned by gradual addition
15 to cold isopropanol (4.0 L). The product was collected by filtration, washed with isopropanol and then dried at room temperature under vacuum (yield – 17.84 g, 92% of the theoretical yield).

EXAMPLE 5b

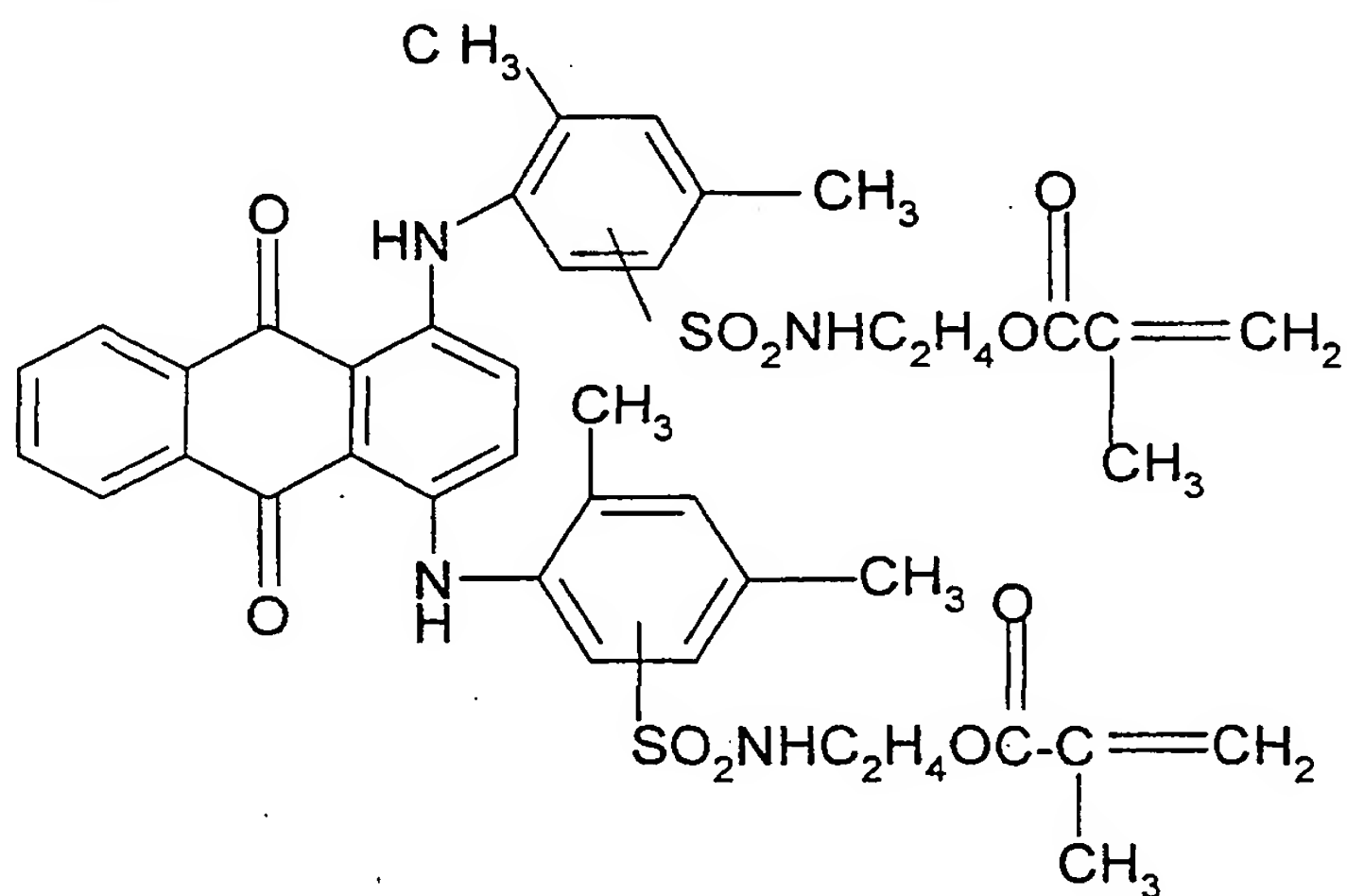
20 A portion (6.43g, 0.01 mol) of the sulfonyl chloride product of Example 5a, acetone (25 ml) and 2-aminoethanol (75 ml) was heated at about 95°C with stirring for 2.5 hours. The reaction mixture was cooled, diluted with 2-ethoxyethanol (175 ml) and then drowned into cold water (800 ml). The dark blue product was

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collected by filtration, washed with hot water and dried in air (yield – 5.39g, 78% of the theoretical yield).

EXAMPLE 5c

5 A portion of the sulfonamide product of Example 5b (1.0g, 0.0014 mol), DMF (10 ml), hydroquinone (10 mg), DMAP (35 mg) and methacrylic anhydride (0.647 ml) were mixed and stirred together. Triethylamine (0.605 ml) was added dropwise and the reaction mixture was then stirred at room temperature for 24 hours and then drowned into water. The solid product was collected by filtration and dried in air (yield – 1.1g, 92% of the theoretical yield). FDMS supported the following structure:

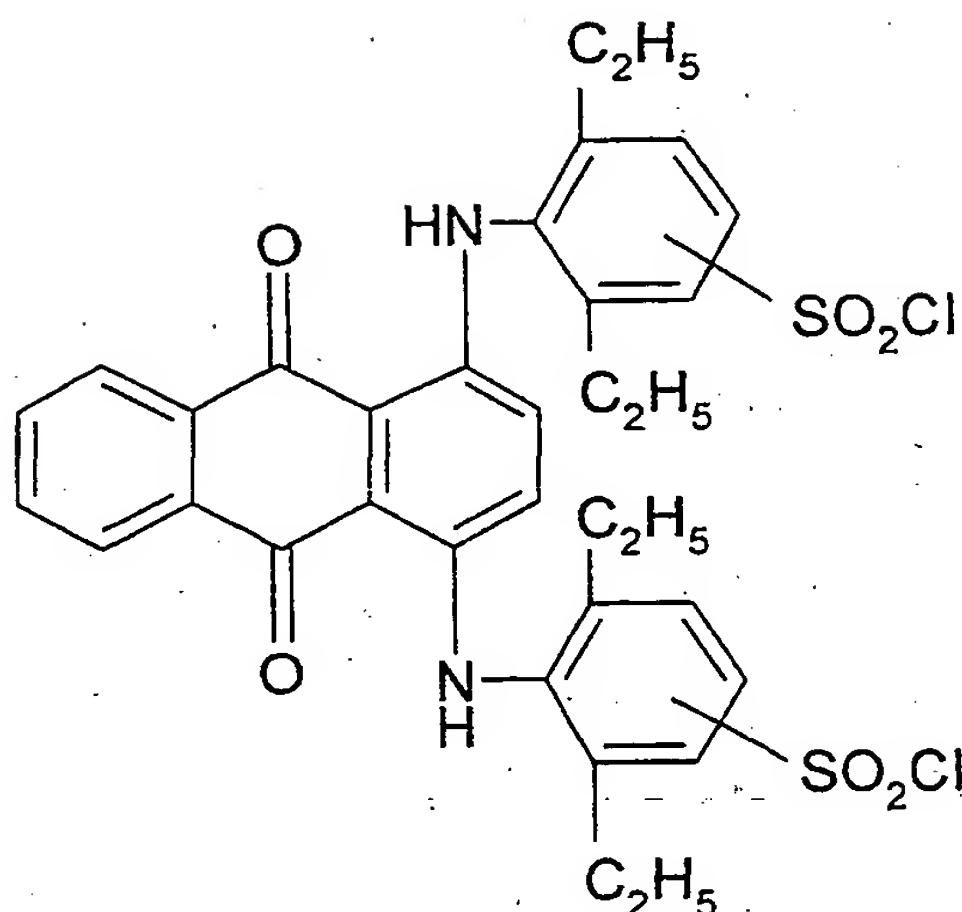


15 An absorption maximum was observed at 630 nm in the UV-visible absorption spectrum in DMF.

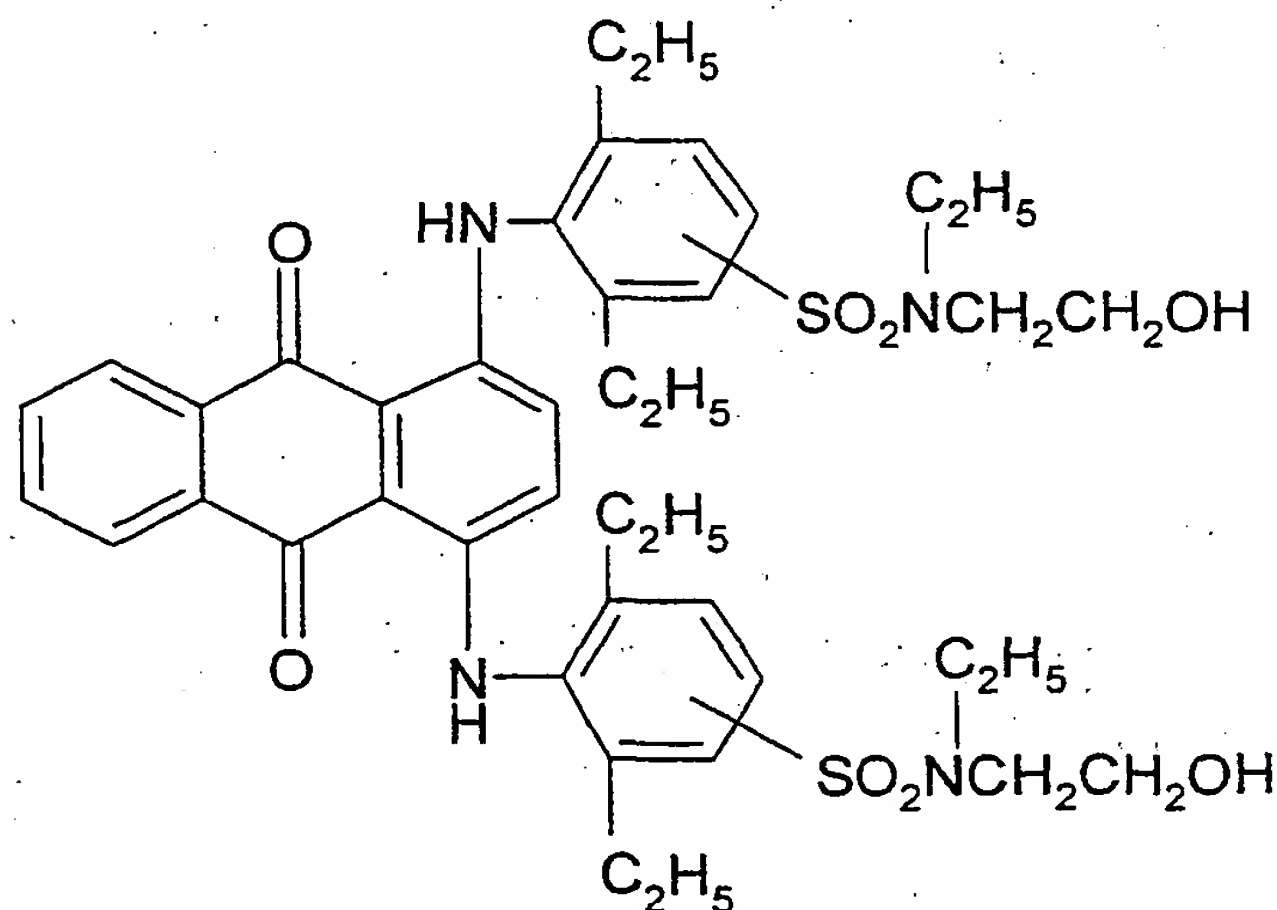
EXAMPLE 6a

20 A mixture of isopropanol (20 ml), N-ethylethanolamine (1.11g, 0.013m) and an anthraquinone disulfonyl chloride prepared by chlorosulfonating 1,4-bis-(2,6-diethylanilino) anthraquinone as described in U.S. Patent 6,121,351, Example 2 (1.75 g, 0.003 mol) having the structure:

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was stirred at room temperature for 3.0 hours. The reaction mixture was drowned
 into a solution of concentrated HCl (10 ml) in water (150 ml). After stirring for
 about 15 minutes, the solid product was collected by filtration, washed well with
 5 water and dried in air (yield – 1.84g, 91.5% of the theoretical yield). FDMS
 supported the following desired structure:

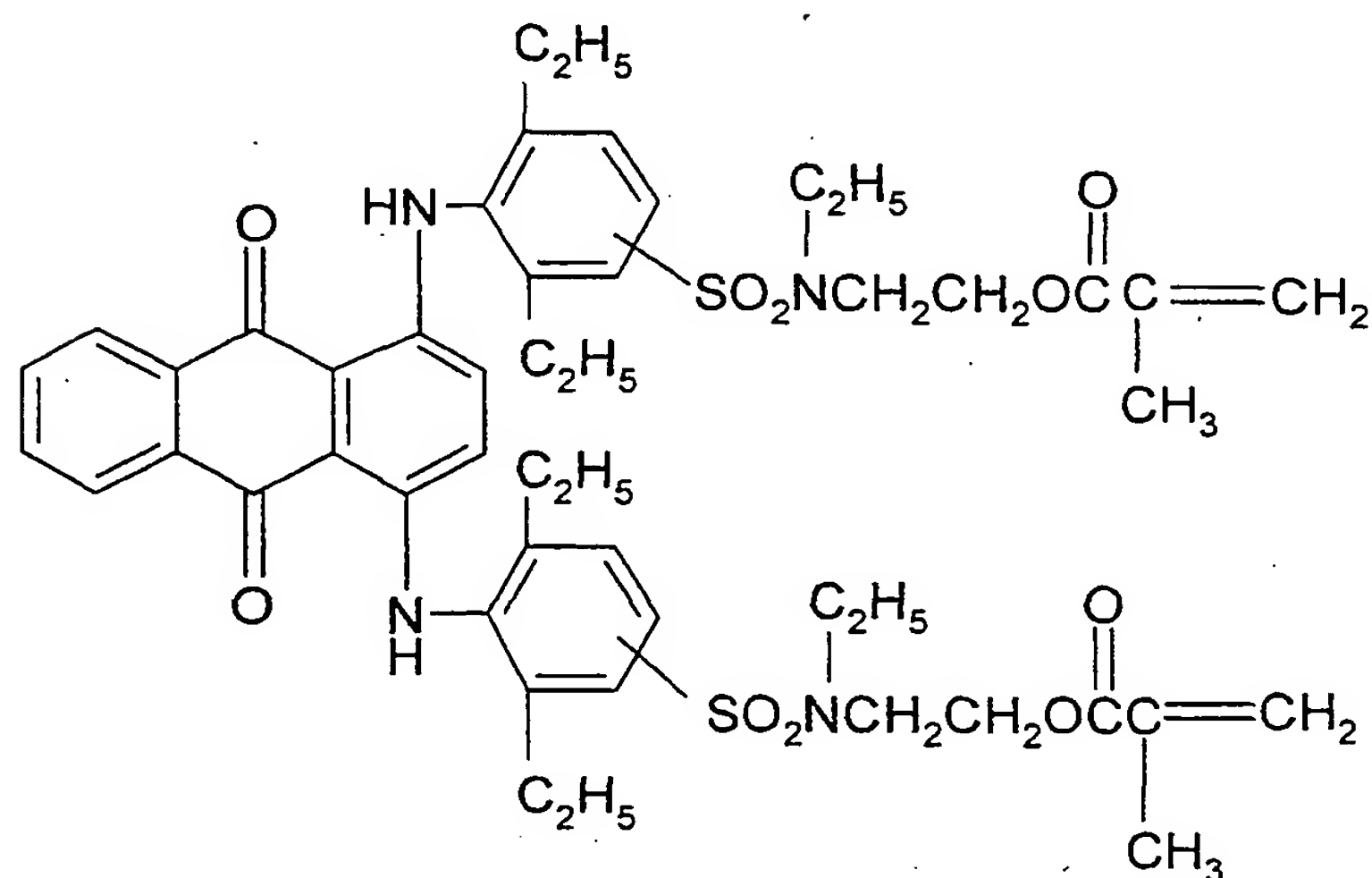


Absorption maxima at 597 nm and 622 nm were observed in the UV-visible
 absorption spectrum in DMF solution.

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EXAMPLE 6b

A portion of the sulfonamide product from Example 6a (1.0g), 0.00124 mol), DMF (25 ml), hydroquinone (10 mg), DMAP (30.3 mg) and methacrylic anhydride (0.556 ml) were mixed together and stirred while triethylamine (0.520 ml) was added dropwise. The reaction mixture was stirred at room temperature for 24 hours and then drowned into water (50 ml). The solid product was collected by filtration and dried in air (yield – 0.96g, 82% of the theoretical yield). FDMS supported the following structure:



An absorption maxima at 579 nm and 623 nm were observed in the UV-Visible light absorption spectrum in DMF as solvent.

EXAMPLE 7

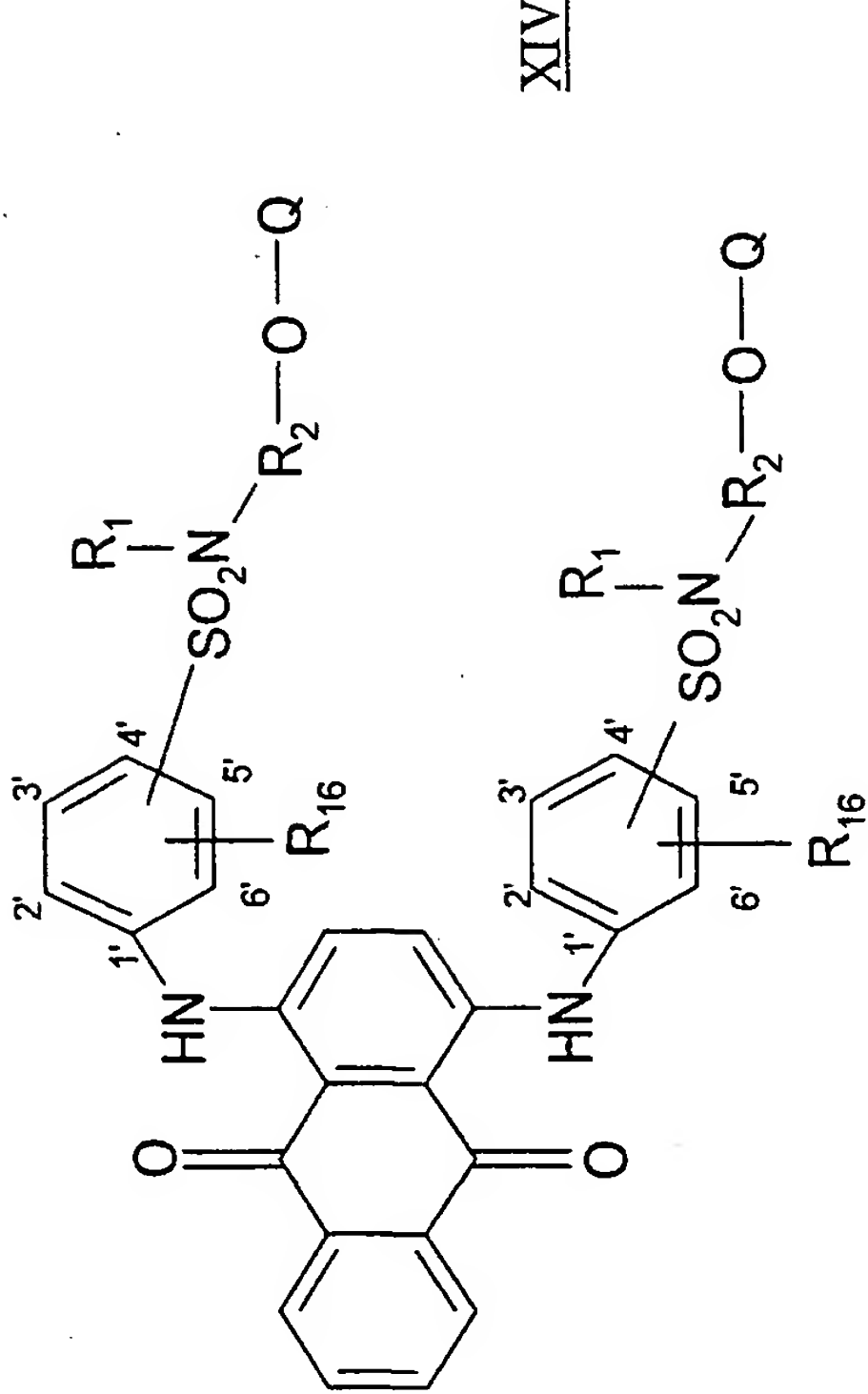
A mixture of the copper phthalocyanine compound (0.100g, 0.0000953 mol) prepared as in Example 1 of U. S. Patent 5,102,980 and having primarily the structure $\text{CuPc}[\text{SO}_2\text{-N-CH}_2\text{C}(\text{CH}_3)_2\text{CH}_2\text{OH}]_{2.5}$, wherein CuPc represents the copper phthalocyanine moiety, DMF (5 ml), hydroquinone (1 mg), DMAP (2.3 mg), methacrylic anhydride (0.071 ml) and triethylamine (0.066 ml) was stirred at room temperature for 24 hours. The reaction mixture was poured into 10 ml of methanol

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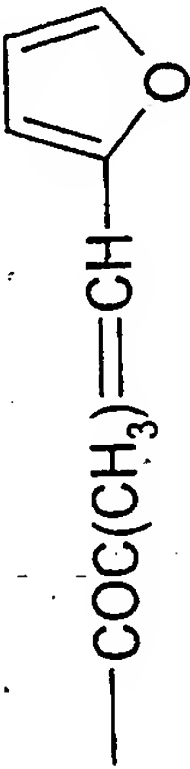
and then water (25 ml) was added. A semi-solid, blue product resulted, which was washed by decantation and then allowed to dry in air. The product consists primarily of the copper phthalocyanine compound having the structure, $\text{CuPc}[\text{SO}_2\text{NHCH}_2\text{C}(\text{CH}_3)_2\text{CH}_2\text{OCO}-\text{C}(\text{CH}_3)=\text{CH}_2]_{2.5}$ and produces a brilliant cyan color when dissolved in DMF.

Additional examples of the thermally-stable, colored, photopolymerizable compounds of the present invention are set forth in the examples of Tables I, II, III, IV, V, VI, VII, VIII and IX. These compounds may be prepared by procedures analogous to those described in the preceding examples and/or by published techniques.

TABLE I
1,4-Bis(arylamino)anthraquinone Colorants of Formula XIV



Example No.	R ₁₆	R ₁	R ₂	Q
8	2',4',6'-tri-CH ₃	CH ₃	-CH ₂ CH ₂ -	-COC(CH ₃)=CH ₂
9	2'-C ₂ H ₅ , 6'-CH ₃	CH ₂ CH ₃	-CH ₂ CH ₂ -	-COCH=CH ₂
10	2',6'-di-C ₂ H ₅	CH ₂ CH ₂ OCO-C(CH ₃)=CH ₂	-CH ₂ CH ₂ -	-COC(CH ₃)-CH ₂

Example No.	R ₁₆	R ₁	R ₂	Q
11	2',6'-di-C ₂ H ₅	H	-CH ₂ CH ₂ OCH ₂ CH ₂ -	-COCH=CH-CH ₃
12	2',6'-di-C ₂ H ₅	H	-CH ₂ CH ₂ (OCH ₂ CH ₂) ₂ -	-COC(CH ₃)=CH ₂
13	2',4',6'-tri-CH ₃	H	-CH ₂ CH ₂ (OCH ₂ CH ₂) ₃ -	-COC(CH ₃)=CH ₂
14	2',4',6'-tri-CH ₃	H	-CH ₂ CH(CH ₃)-	-COCOCH=CHC ₆ H ₅
15	2',6'-diBr,4'-CH ₃	H	-CH ₂ -1,4-C ₆ H ₁₀ -CH ₂ -	-COC(CH ₃)=CH ₂
16	2'-Br, 4',6'-di-CH ₃	H	(CH ₂) ₄	
17	2'OCH ₃	H	(CH ₂) ₆	-COCH=CH-CO ₂ CH ₃
18	4',-CH ₃	H	-CH ₂ CH(OH)CH ₂ -	-CONHCOC(CH ₃)=CH ₂
19	2'-OCH ₃ , 5'-CH ₃	H	-1,4-C ₆ H ₄ -	-CONHC(CH ₃) ₂ OCOCH=CH ₂
20	4'-OCH ₃	H	-1,4-C ₆ H ₁₀ -	-COC(CH ₃) ₂ NHCOC(CH ₃)=CH ₂
21	2',6'-diC ₂ H ₅	H	-CH ₂ CH(C ₆ H ₅)-	-CO-1,4-C ₆ H ₄ -CH=CH ₂
22	2',6'-diC ₂ H ₅	H	-CH ₂ CH(OCH ₃)CH ₂ -	CONHC(CH ₃) ₂ -1,3-C ₆ H ₄ -CH=CH ₂

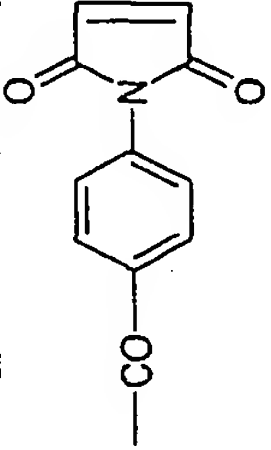
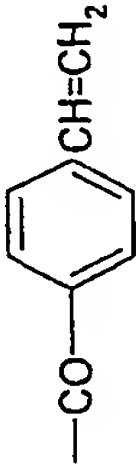
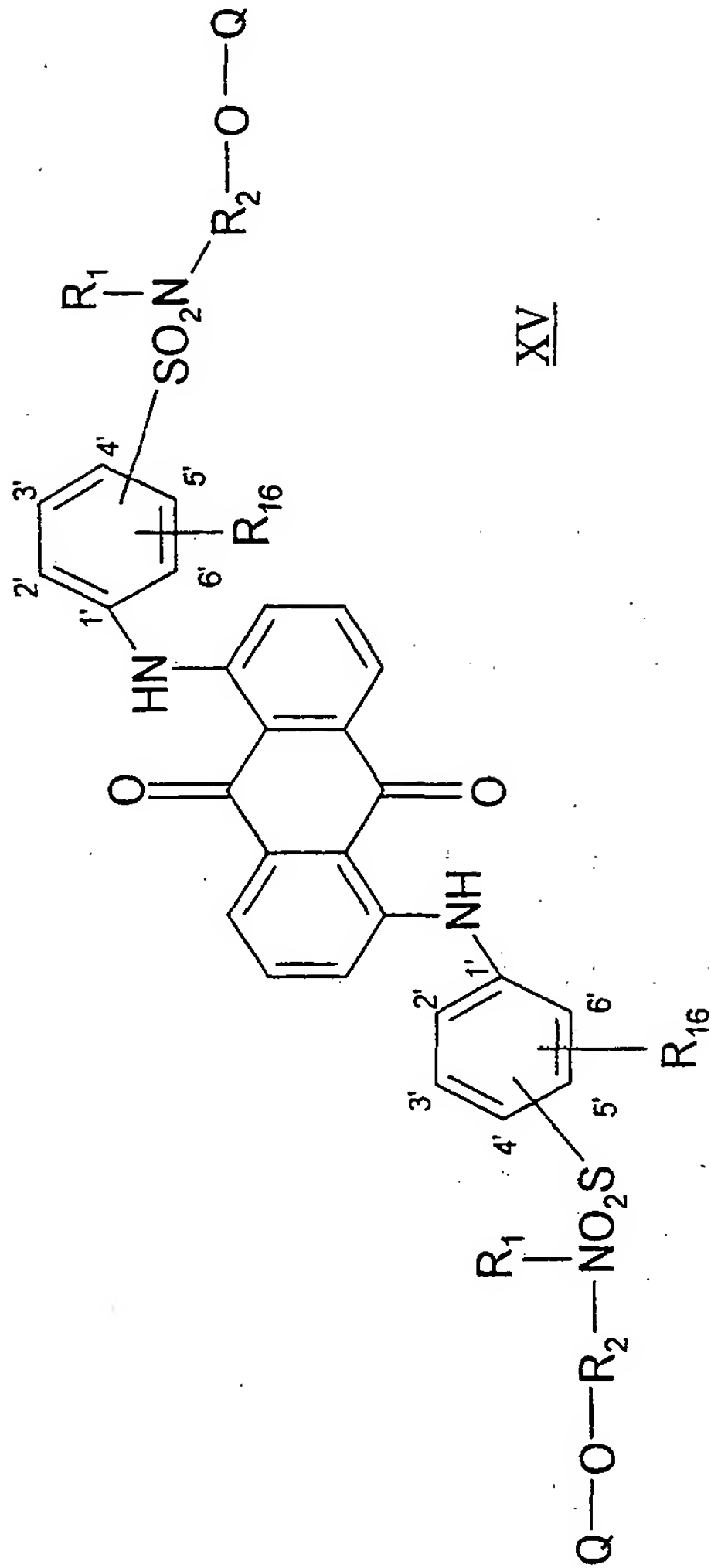
Example No.	R ₁₆	R ₁	R ₂	Q
23	2',6'-diC ₂ H ₅	C ₆ H ₅	-CH ₂ CH ₂ -	
24	2',6'-diC ₂ H ₅	C ₆ H ₁₁	-CH ₂ CH ₂ -	-COCH ₂ C(=CH ₂)CO ₂ CH ₃
25	2',6'-diC ₂ H ₅	CH ₂ C ₆ H ₅	-CH ₂ CH ₂ -	
26	2',6'-diC ₂ H ₅	CH ₂ CH ₂ OCO-NHCOC(CH ₃)=CH ₂	-CH ₂ CH ₂ -	-CONHCOC(CH ₃)=CH ₂

TABLE II
1,5-Bis(arylamino)anthraquinone Colorants of Formula XV



Example No.	R ₁₆	R ₁	R ₂	Q
27	2'-OCH ₃	H	-CH ₂ CH ₂ -	-COC(CH ₃)=CH ₂
28	2'-OCH ₃	-CH ₂ CH ₂ OCO- C(CH ₃)=CH ₂	-CH ₂ CH ₂ -	-COC(CH ₃)=CH ₂
29	2'-OC ₂ H ₅	H	-(CH ₂) ₃	-COCH=CH ₂
30	2'-OC ₂ H ₅	-CH ₃	-CH ₂ CH ₂ -	-COC(CH ₃)=CH ₂
31	2'-OCH(CH ₃) ₂	-C ₂ H ₅	-CH ₂ CH ₂ -	-CONHCOC(CH ₃)=CH ₂

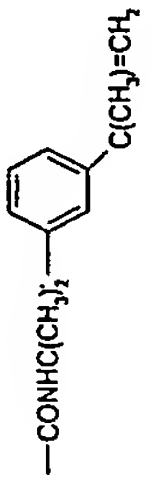
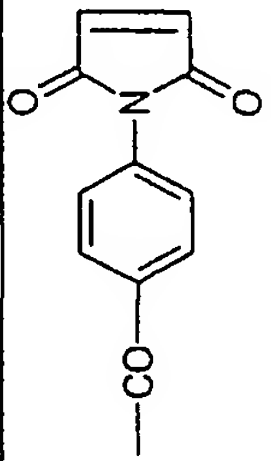
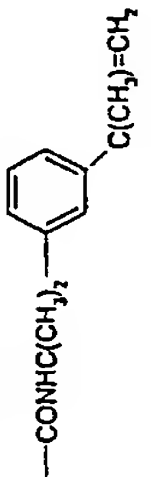
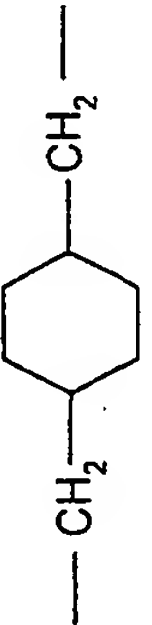
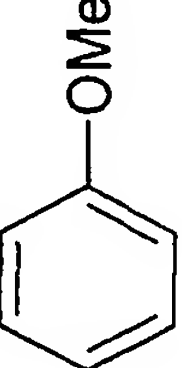
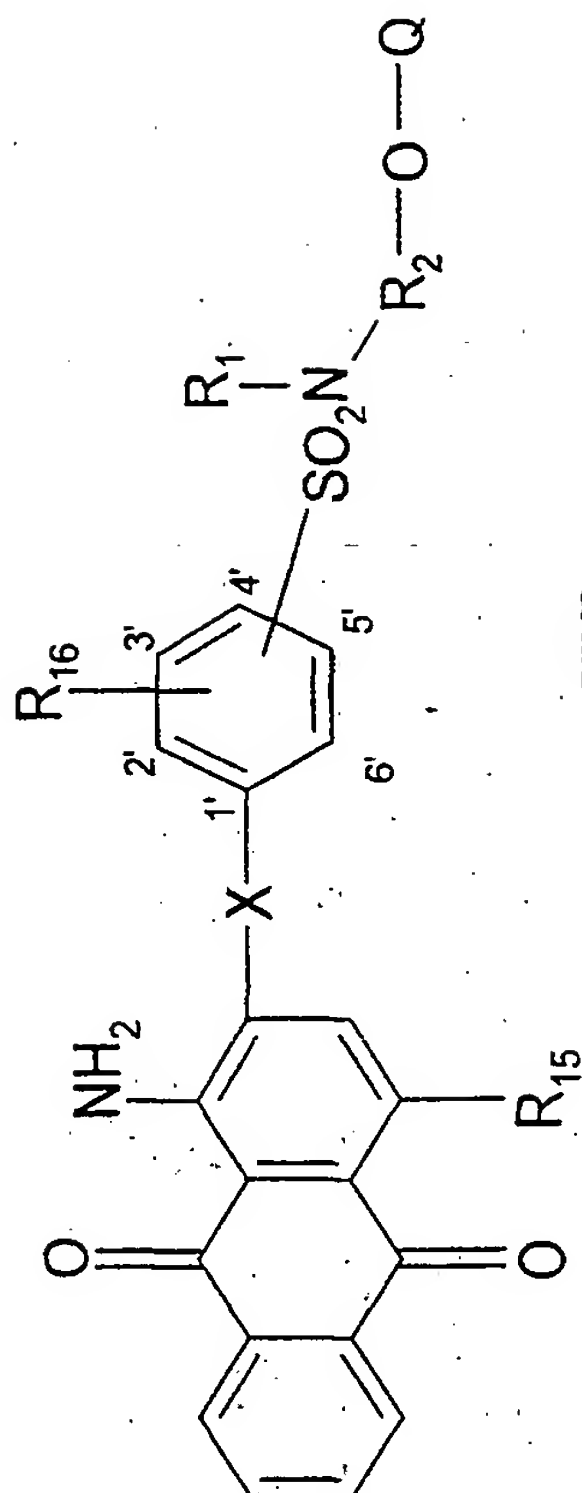
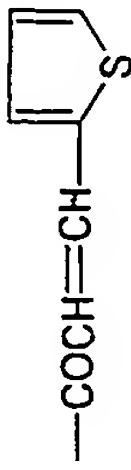
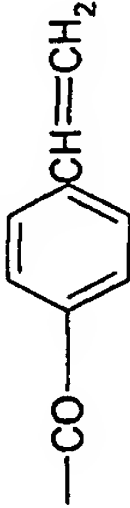
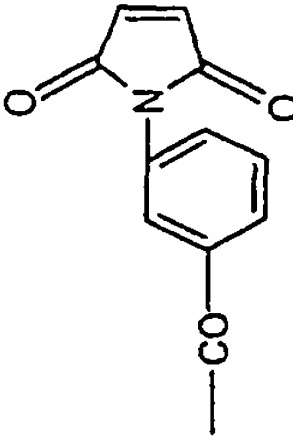
Example No.	R ₁₆	R ₁	R ₂	Q
32	2'-OCH(CH ₃) ₂	H	—(CH ₂) ₆ —	
33	2'-OC ₄ H _{9-n}	H	—CH ₂ CH(CH ₃)—	—CONH(CH ₂) ₆ OCOC(CH ₃)=CH ₂
34	2'-OCH ₃ , 5'-CH ₃	—C ₆ H ₅	—CH ₂ CH ₂ —	—COC(CH ₃) ₂ NHCOCH=CH ₂
35	2'OCH ₃ , 5'-Cl	—C ₆ H ₁₁	—CH ₂ CH ₂ —	
36	2', 6'-diC ₂ H ₅	H	—CH ₂ CH ₂ —	—COC(CH ₃)=CH ₂
37	4'-OCH ₃	—CH ₂ C ₆ H ₅	—CH ₂ CH ₂ —	
38	2'-OCH ₃	H	—CH ₂ CH ₂ OCH ₂ CH ₂ —	—COCH=CH ₂
39	2'-OCH ₃	H	—CH ₂ CH ₂ (OCH ₂ CH ₂) ₂ —	—COC(CH ₃)=CH ₂
40	2'-OCH ₃	H	—CH ₂ CH ₂ (OCH ₂ CH ₂) ₃ —	—COC(CH ₃)=CH ₂
41	2'-OCH ₃	H		—COCH=CH— 

TABLE III
1,2,4-Trisubstituted Anthraquinone Colorants of Formula XVI



XVI

Example No.	R ₁₅	R ₁₆	X	R ₁	R ₂	Q
42	-OH	H	O	H	-CH ₂ CH ₂ -	-COC(CH ₃)=CH ₂
43	-OH	H	O	-CH ₂ CH ₂ O- COC(CH ₃)=CH ₂	-CH ₂ CH ₂ -	-COC(CH ₃)=CH ₂
44	-OH	H	S	-C ₂ H ₅	-CH ₂ CH ₂ -	-COCH=CH ₂
45	-OH	H	S	-CH ₃	-CH ₂ CH ₂ -	-CONHC(CH ₃) ₂ -C ₆ H ₄ -C(CH ₃)=CH ₂
46	-OH	2'- OCH ₃	O	-C ₆ H ₅	-CH ₂ CH ₂ -	COCH=CH-C ₆ H ₅

Example No.	R ₁₅	R ₁₆	X	R ₁	R ₂	Q
47	-OH	4'OCH ₃	O	-CH ₃	-CH ₂ CH ₂ -	
48	-OH	4'CH ₃	S	H	-(CH ₂) ₄	-COCH=CH=CO ₂ H
49	-OH	3'OCH ₃	S	H	-CH ₂ CH ₂ OCH ₂ CH ₂ -	-COCH=CH-CH ₃
50	-NHSO ₂ CH ₃	H	O	H	-CH ₂ CH ₂ (OCH ₂ CH ₂) ₂ -	-COC(CH ₃)=CH ₂
51	-NHSO ₂ C ₆ H ₅	H	O	-CH ₂ CH ₂ O- COCH=CH ₂	-CH ₂ CH ₂ -	-COCH=CH ₂
52	-NHSO ₂ C ₆ H ₁₁	H	S	H	-CH ₂ CH ₂ (OCH ₂ CH ₂) ₃ -	-COC(CH ₃)=CH ₂
53	-NHCOC ₆ H ₅	H	O	-C ₂ H ₅	-CH ₂ CH ₂ -	-CONHCOC(CH ₃)=CH ₂
54	-NH ₂	H	O	-C ₂ H ₅	-(CH ₂) ₆	-COC(CH ₃)=CH ₂
55	-NHC ₂ H ₅	H	S	-C ₆ H ₅	-CH ₂ CH ₂ -	
56	-SC ₂ H ₅	H	S	-C ₆ H ₁₁	-CH ₂ CH ₂ -	
57	NHCONHC ₂ H ₅	H	O	H	-CH ₂ CH(OH)CH ₂ -	-COCH=CH ₂

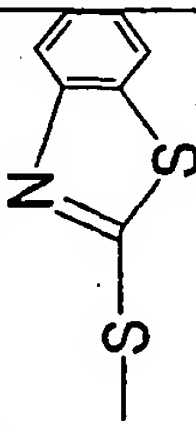
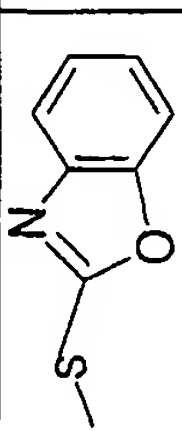
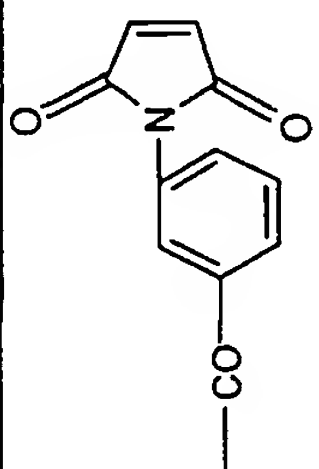
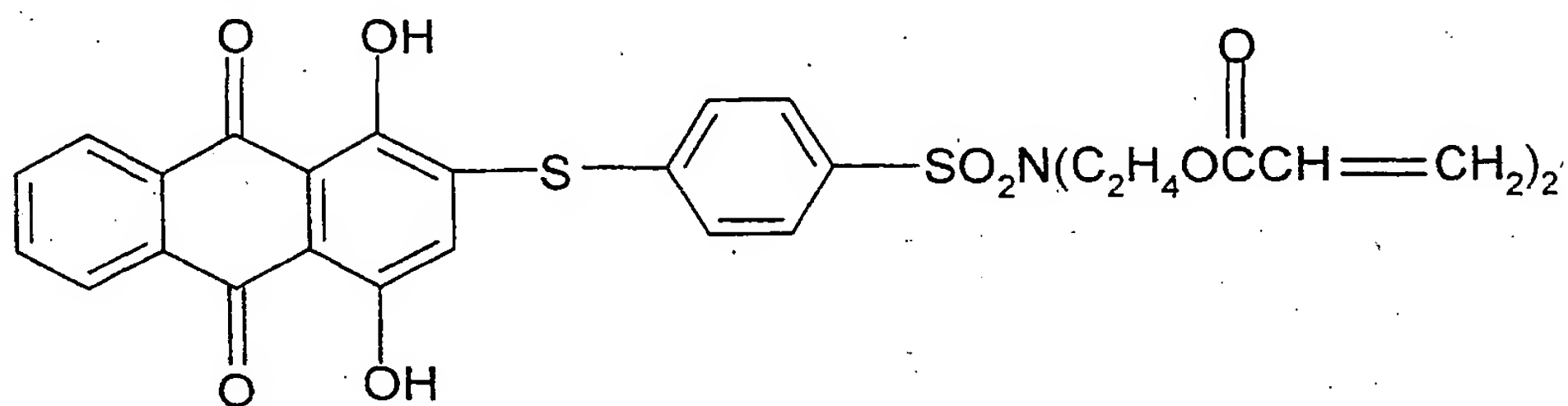
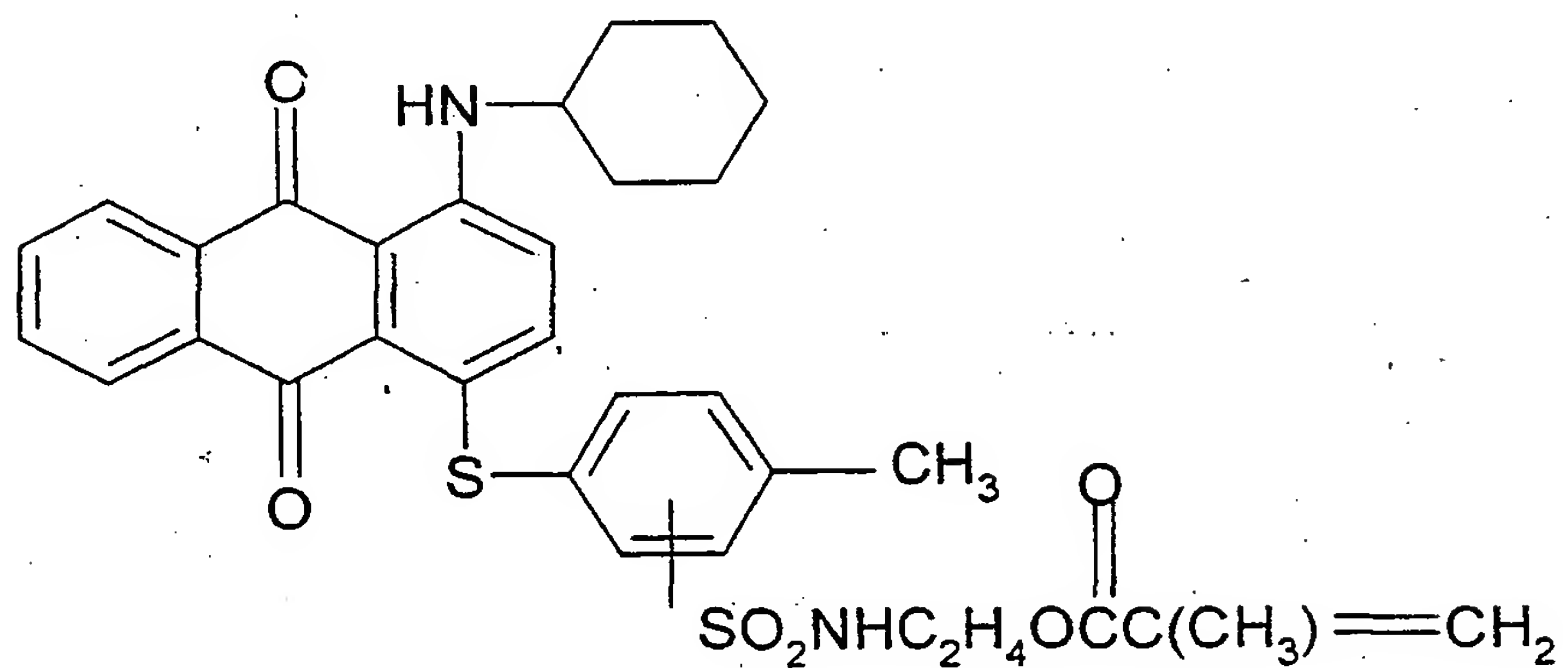
Example No.	R15	R16	X	R1	R2	Q
64	-SO ₂ C ₆ H ₅	2'-OCH ₃	NH	H	-CH ₂ CH ₂ OCH ₂ CH ₂ -	-COCH=CH-CO ₂ C ₂ H ₅
65	-SC ₆ H ₅	2'-OCH ₃	NH	H	-CH ₂ CH ₂ (OCH ₂ CH ₂) ₂ -	-COCH=CH ₂
66		2'-OCH ₃	NH	H	-CH ₂ CH ₂ (OCH ₂ CH ₂) ₃ -	-COC(CH ₃)=CH ₂
67		2'-OCH ₃	NH	H	-CH ₂ CH(OH)CH ₂ -	-COC(CH ₃)=CH ₂
68	-SC ₂ H ₅	2'-OCH ₃	NH	H	-CH ₂ CH(CH ₃)-	
69	-Br	4'-CH ₃	S	H	-CH ₂ OH(C ₆ H ₅)-	-COCH=CH ₂
70	-SC ₂ H ₅	4'-CH ₃	S	H	-CH ₂ CH ₂ -	-COC(CH ₃)=CH ₂
71	-OCH ₃	4'-CH ₃	S	H	-(CH ₂) ₃	-COC(CH ₃)=CH ₂
72	-OC ₄ H _{9-n}	4'-CH ₃	S	-C ₄ H _{9-n}	-CH ₂ CH ₂ -	-COCH=CH ₂
73	-SO ₂ N(CH ₃) ₂	4'-CH ₃	S	H	-CH ₂ CH ₂ -	-COCH=CH-CH ₃
74	-CF ₃	4'-CH ₃	S	H	-CH ₂ CH ₂ -	-COC(CH ₃)=CH ₂

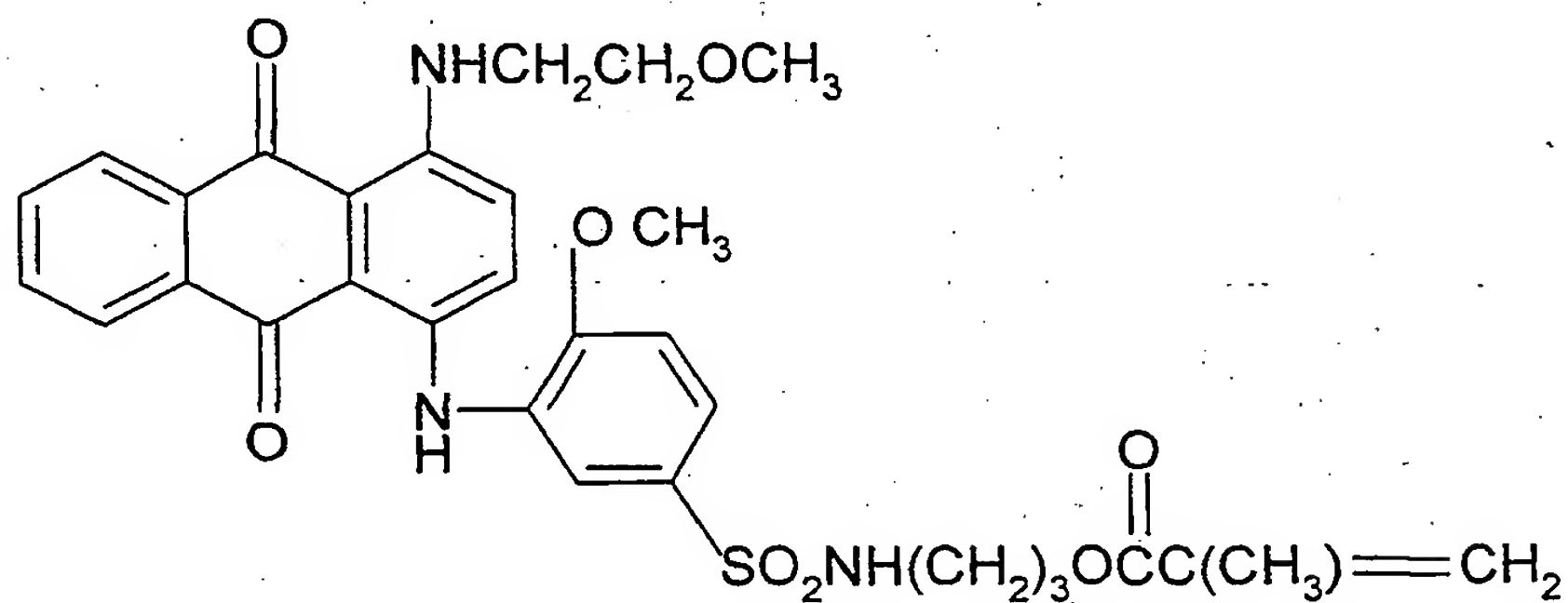
Table V

Miscellaneous Anthraquinone Colorant FormulasEXAMPLE 75

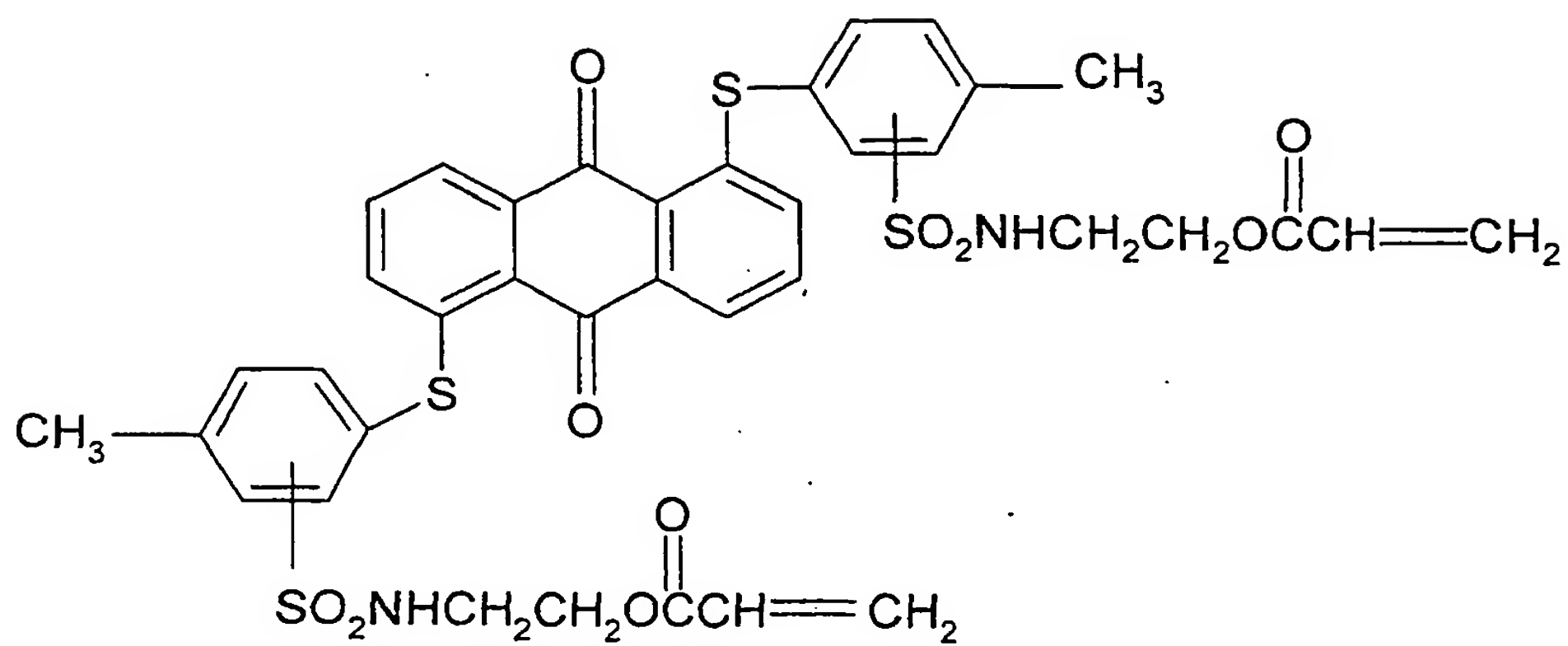
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EXAMPLE 76EXAMPLE 77

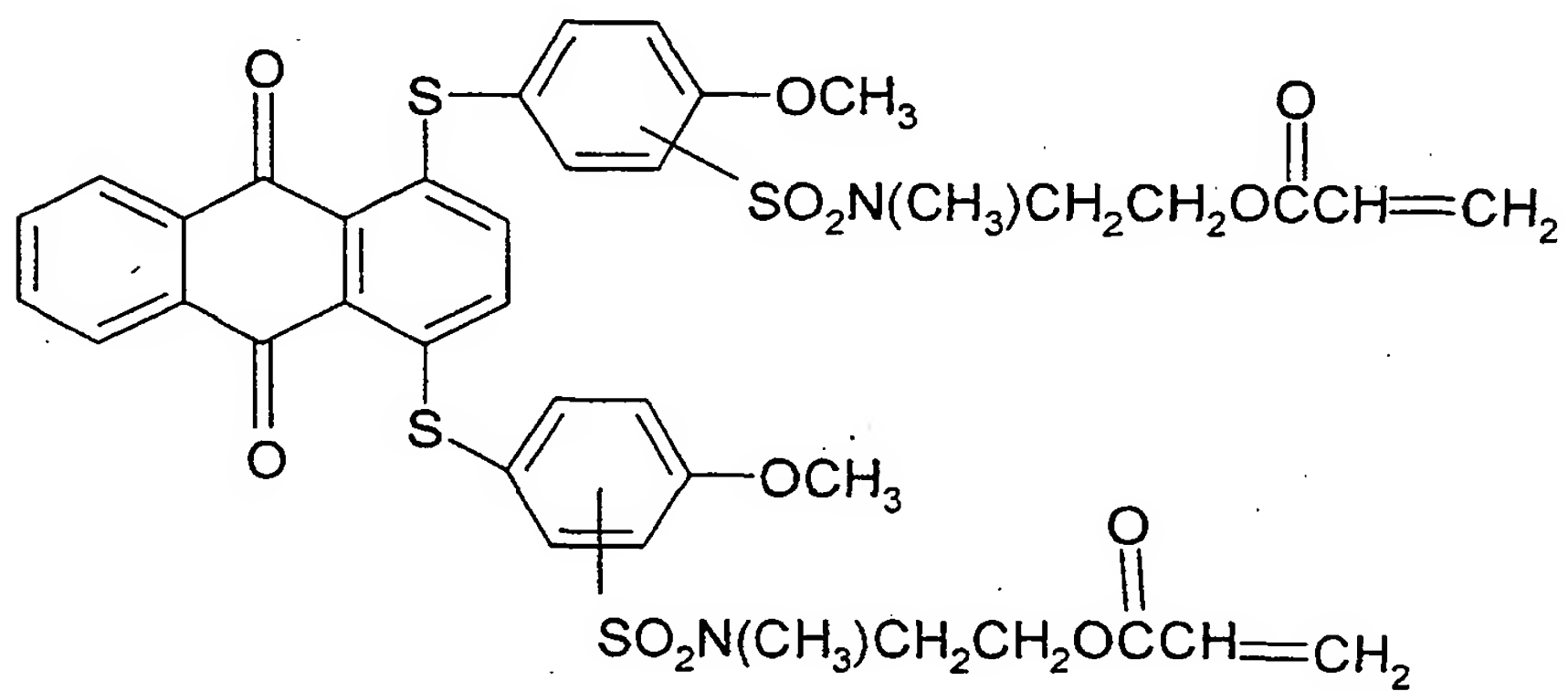
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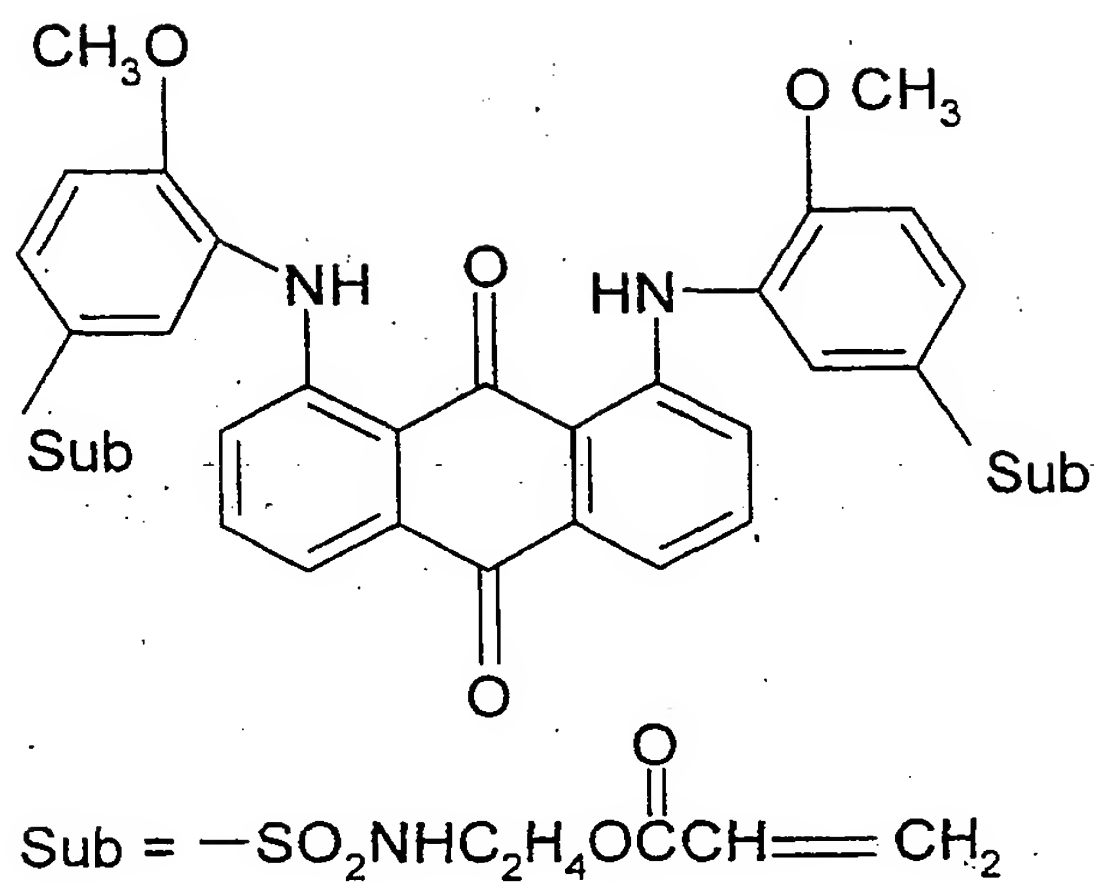
EXAMPLE 78EXAMPLE 79

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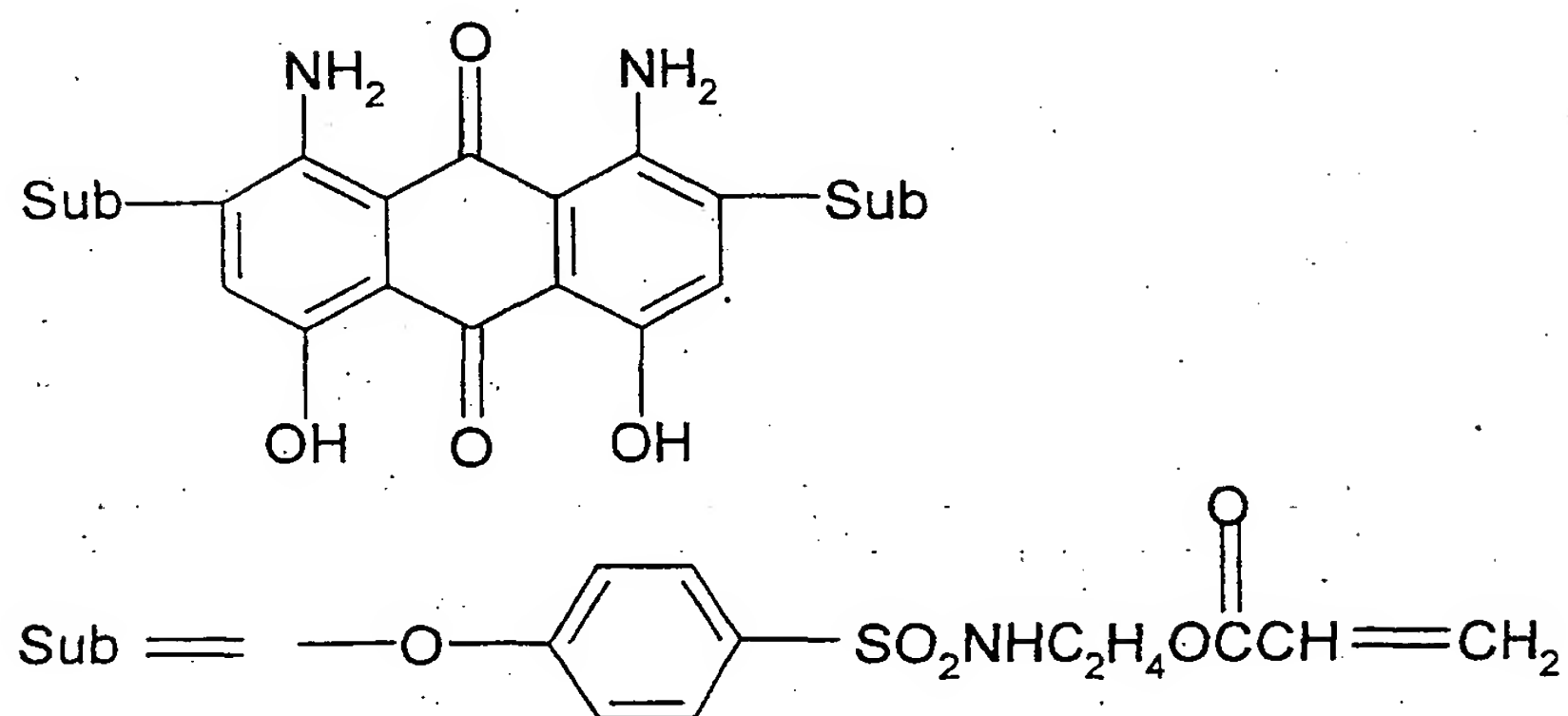


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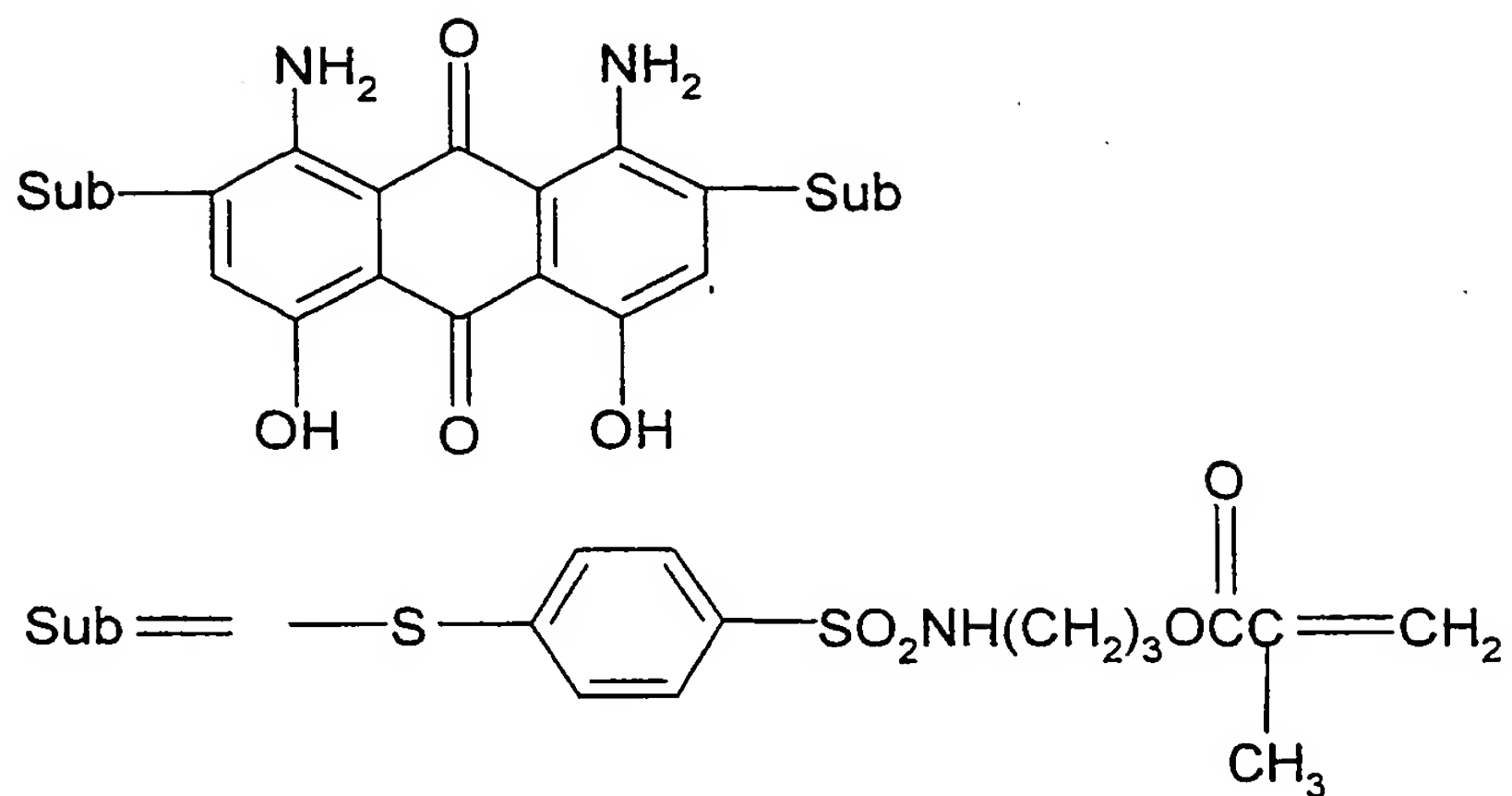
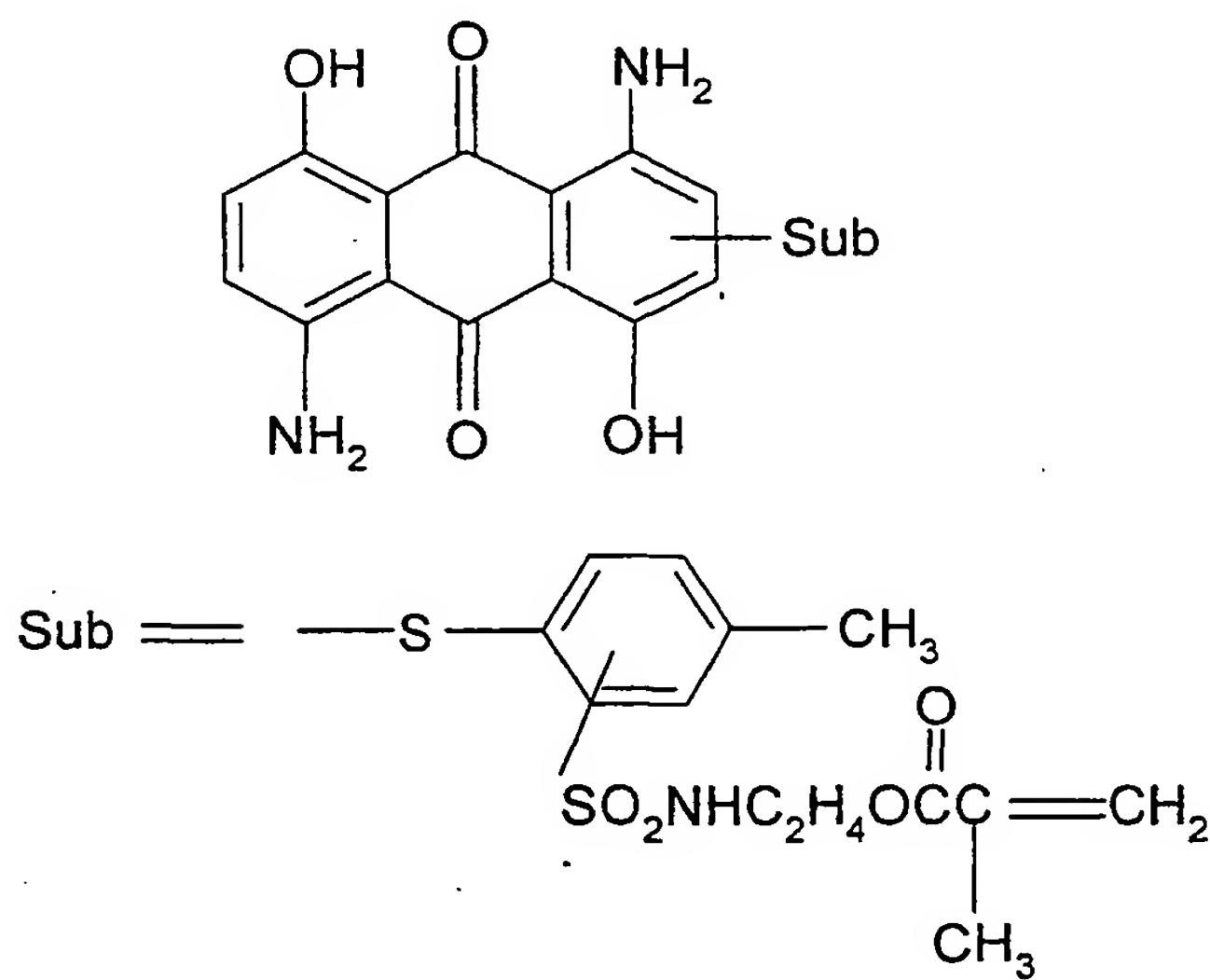
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EXAMPLE 80

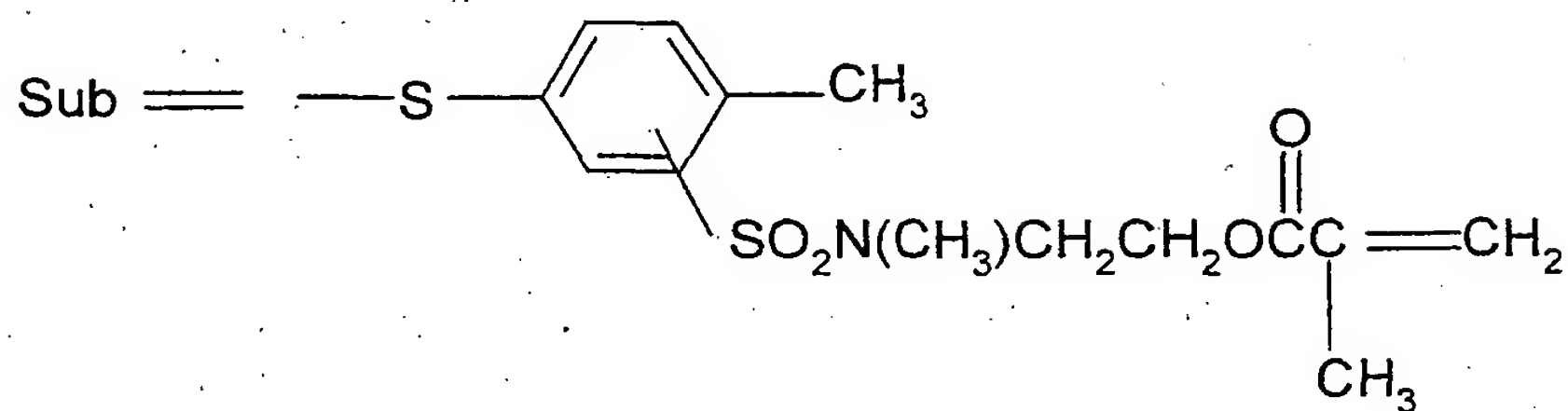
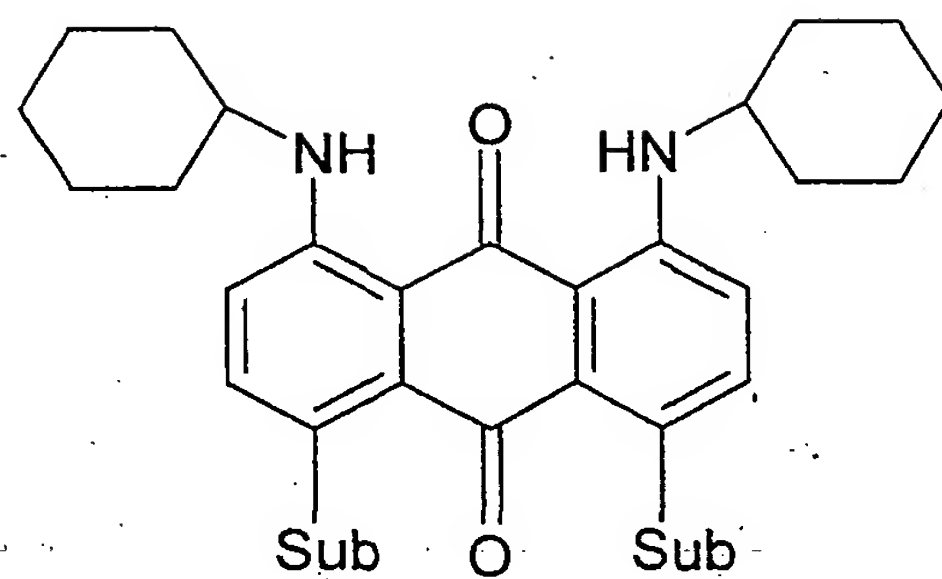
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EXAMPLE 81

- 32 -

EXAMPLE 82EXAMPLE 83

- 33 -

EXAMPLE 84

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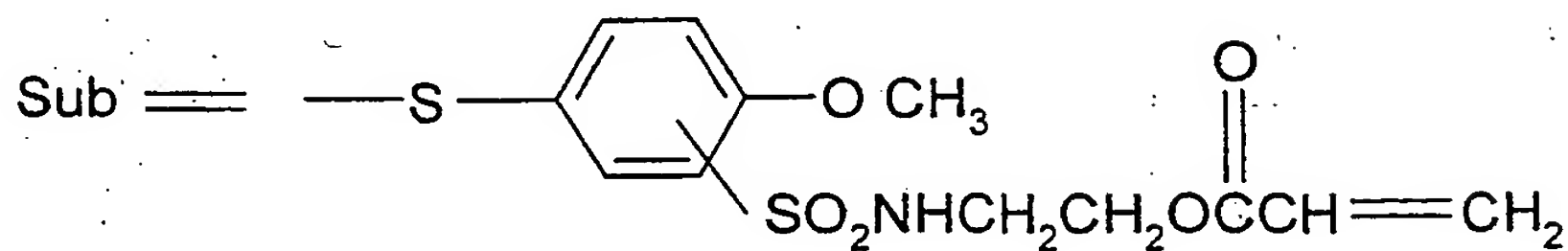
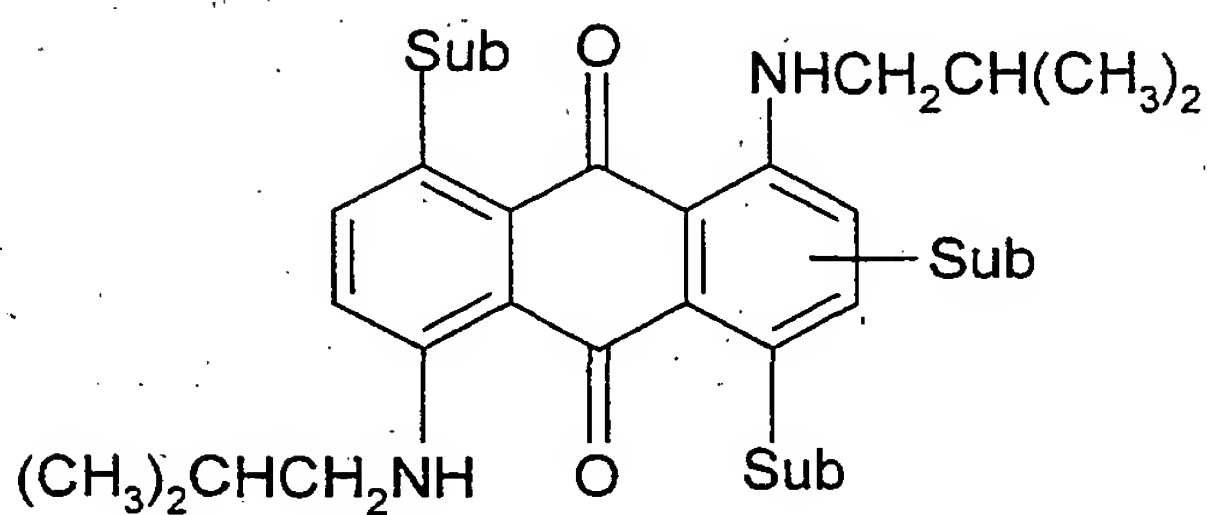
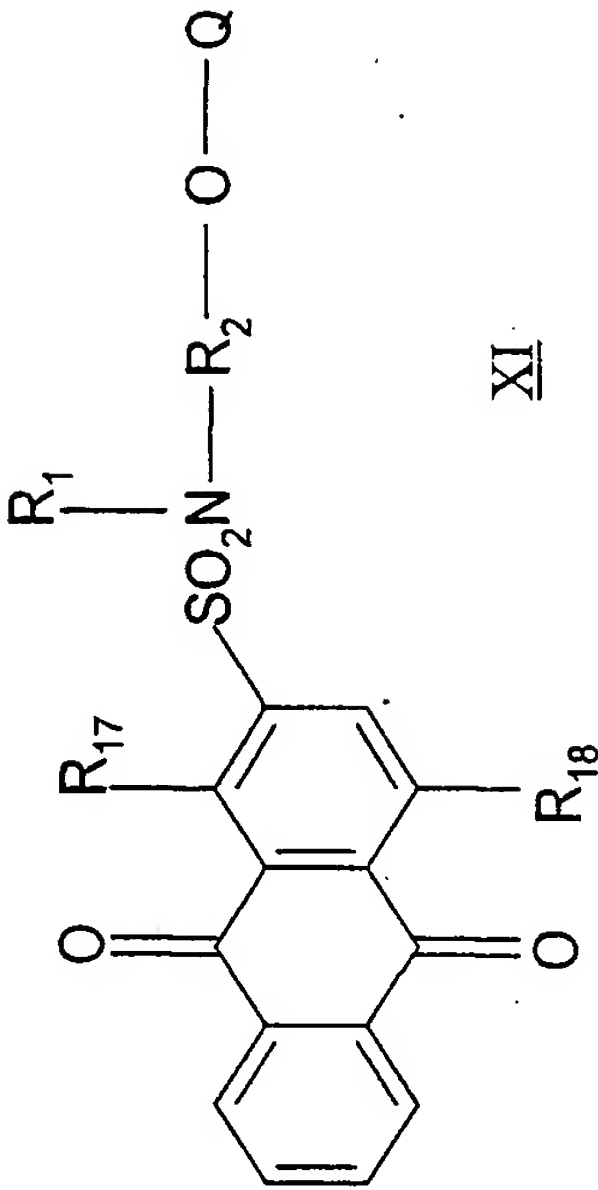
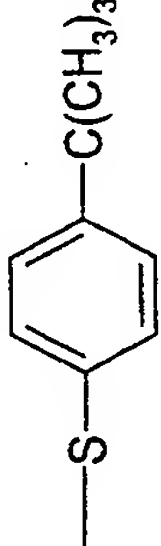
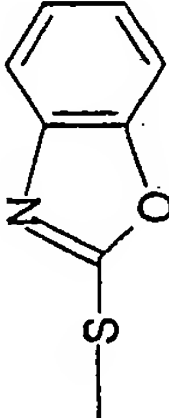
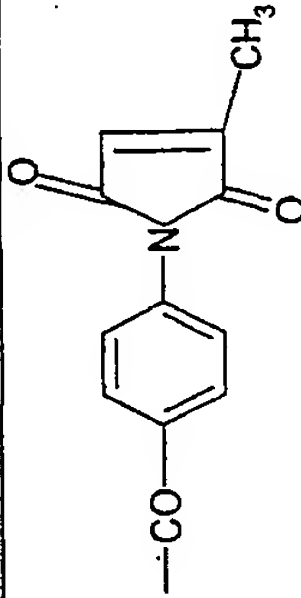
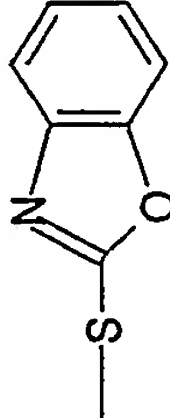
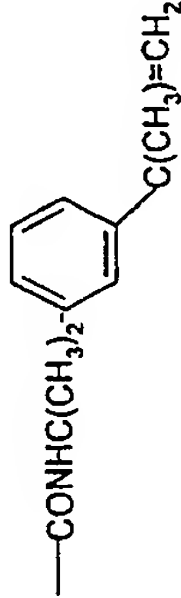
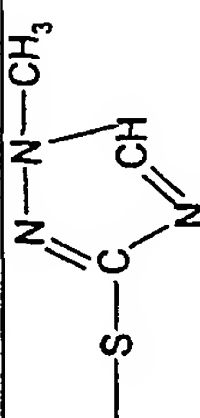
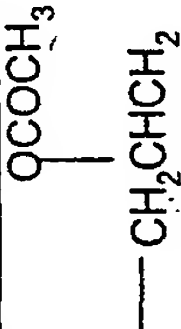
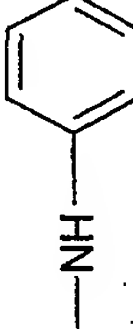
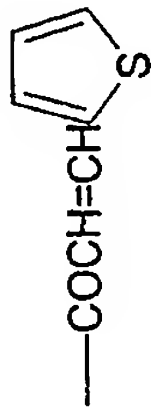
EXAMPLE 85

TABLE VI
Anthraquinone Compounds of Formula XI



Example No.	R ₁₇	R ₁₈	R ₁	R ₂	Q
86	-NH ₂	Br	H	-CH ₂ CH ₂ -	-COC(CH ₃)=CH ₂
87	-NH ₂	-S-C ₆ H ₅	-CH ₂ CH ₂ O- COC(CH ₃)=CH ₂	-CH ₂ CH ₂ -	-COC(CH ₃)=CH ₂
88	-NH ₂		H	-(CH ₂) ₄ -	-COCH=CH-CH ₃

Example No.	R ₁₇	R ₁₈	R ₁	R ₂	Q
89	-NH ₂		-CH ₃	-CH ₂ CH ₂ OCH ₂ CH ₂ -	-COCH=CH-C ₆ H ₅
90	-NH ₂		-C ₂ H ₅	-CH ₂ CH ₂ (OCH ₂ CH ₂) ₂ -	
91	-NH ₂		-C ₆ H ₅	-CH ₂ CH ₂ (OCH ₂ CH ₂) ₂ -	
92	-NH ₂		-C ₅ H ₉	-CH ₂ CH(OH)CH ₂ -	-CONHCOC(CH ₃)=CH ₂
93	-NH ₂	-SCH ₂ CH ₂ OCOCCH ₃	H	 -CH ₂ CHCH ₂ -	-COCH=CH ₂
94	-NH ₂		H	-CH ₂ CH(CH ₃)-	

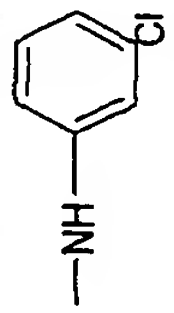
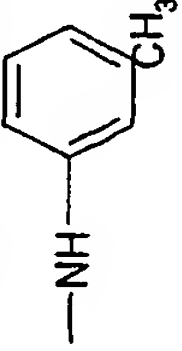
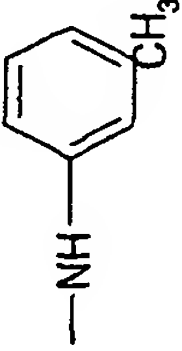
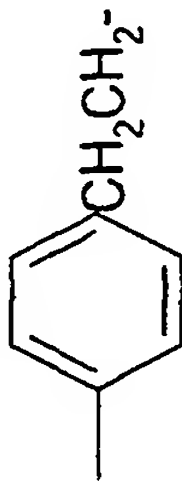
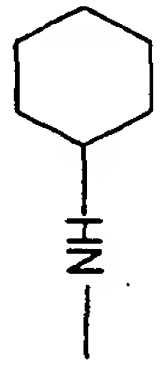
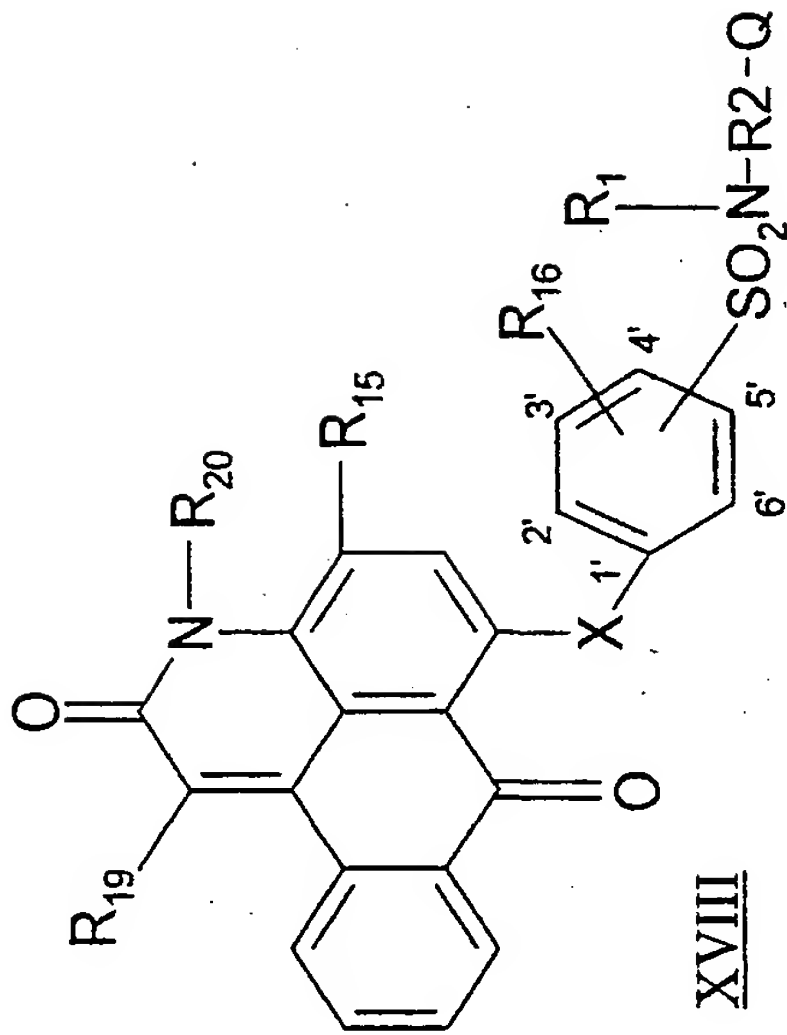
Example No.	R ₁₇	R ₁₈	R ₁	R ₂	Q
95	-NH ₂		H	$-(CH_2)_6-$	$\begin{array}{c} \text{CH}_2 \\ \parallel \\ -COCCH_2CO_2CH_3 \end{array}$
96	-NH ₂		H	$-CH_2CH(C_6H_5)-$	$-COC(CH_3)=CH_2$
97	-NH ₂		H		$-COCH=CH_2$
98	-NH ₂		H	$-CH_2CH_2-$	$-COC(CH_3)=CH_2$

TABLE VII
Anthrapyridone Colorants of Formula XVIII



Example No.	R ₁₅	R ₁₆	X	R ₁₉	R ₂₀	R ₁	R ₂	Q
99	H	H	NH	H	-CH ₃	-CH ₂ CH ₂ O- C(CH ₃)CH ₂ CH ₃	-CH ₂ CH ₂ -	-COC(CH ₃)=CH ₂
100	H	4'-CH ₃	NH	-CN	-CH ₂ CH ₃	H	-CH ₂ CH ₂ -	-COCH=CH ₂
101	-CH ₃	4'-CH ₃	NH	-CN	H	-CH ₃	(CH ₂) ₃	-COCH=CH-CH ₃
102	H	4'-CH ₃	NH	CO ₂ C ₂ H ₅	-CH ₃	-CH ₂ CH ₃	(CH ₂) ₄	-COCH=CH-CO ₂ H
103	-Br	4'-CH ₃	NH	CO ₂ C ₂ H ₅	H	-CH ₂ CH ₂ O- C(CH ₃)CH ₂ CH ₃	-CH ₂ CH ₂ -	-COC(CH ₃)=CH ₂
104	-S-C ₆ H ₅	4'-CH ₃	NH	CO ₂ C ₂ H ₅	H	-C ₆ H ₅	-CH ₂ CH ₂ -	

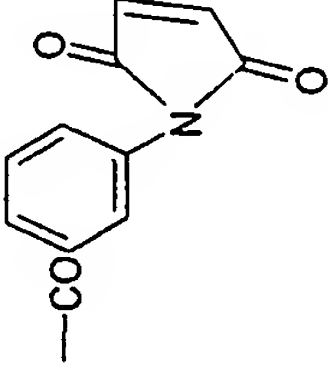
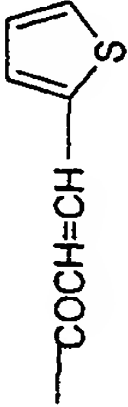
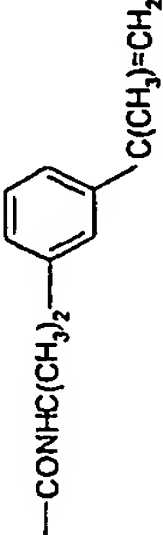
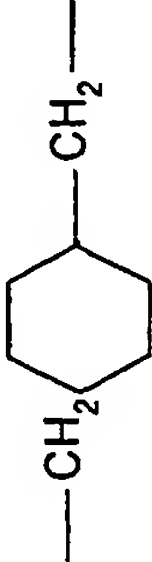
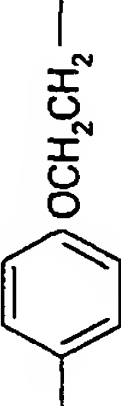
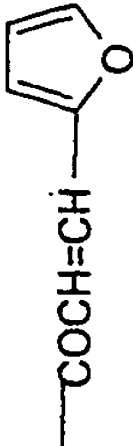
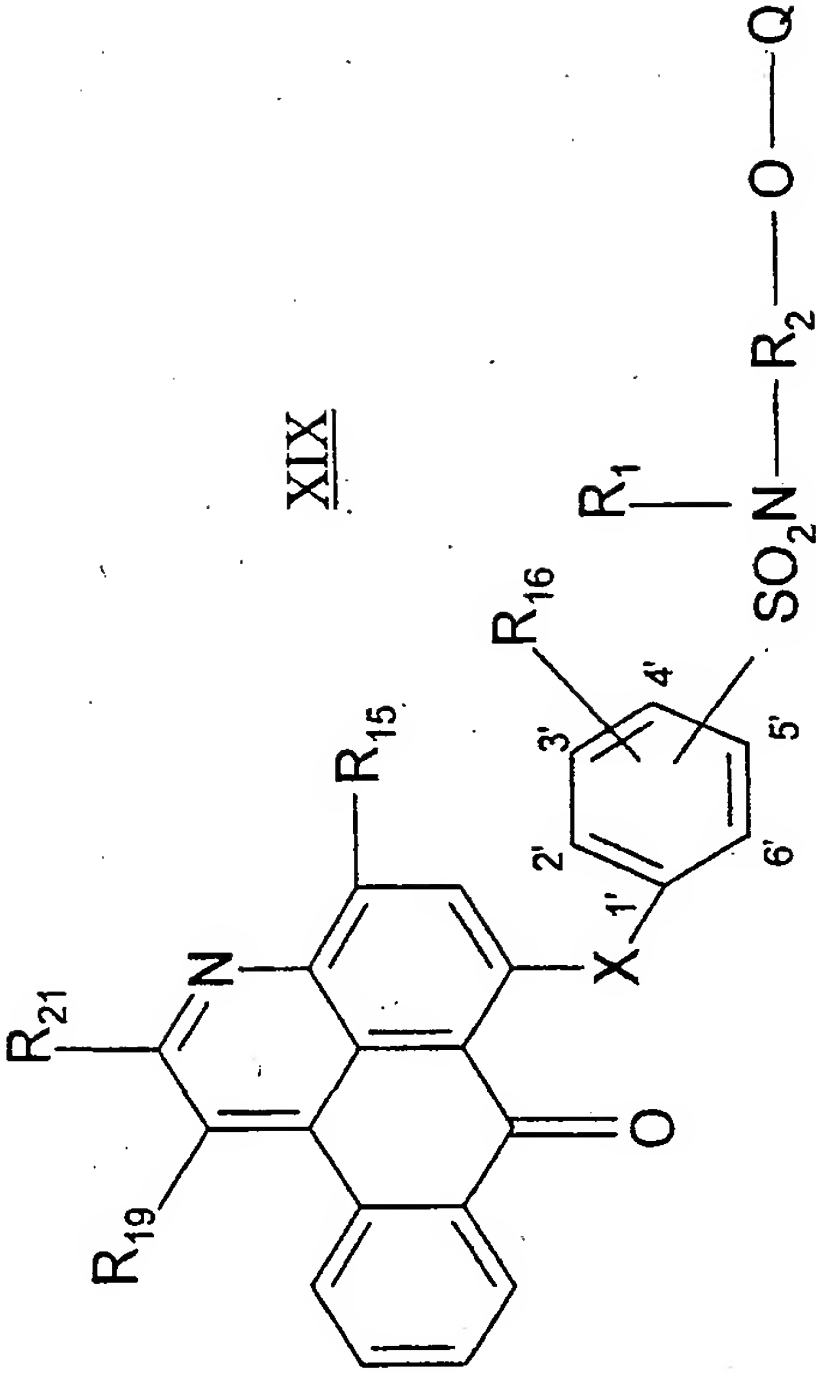
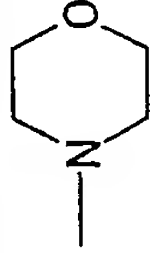
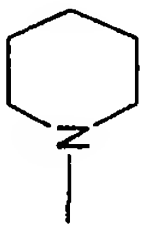
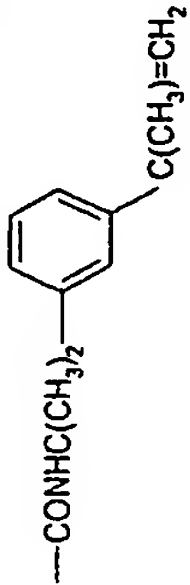
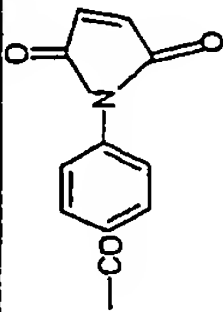
Example No.	R ₁₅	R ₁₆	X	R ₁₉	R ₂₀	R ₁	R ₂	Q
105	-SO ₂ C ₆ H ₅	4'-CH ₃	NH	CO ₂ C ₂ H ₅	H	H	-CH ₂ CH ₂ OCH ₂ CH ₂ -	
106	-OC ₆ H ₅	H	NH	CO ₂ C ₂ H ₅	H	-C ₄ H ₉ -n	-CH ₂ CH ₂ (OCH ₂ CH ₂) ₂ -	
107	H	4'C ₂ H ₅	S	-COC ₆ H ₅	-CH ₂ C ₆ H ₅	H	-CH ₂ CH(CH ₃)-	-COCH=CH-C ₆ H ₅
108	H	2'-CH ₃	S	-COCH ₃	-CH ₂ CH(CH ₃) ₂	H	-CH ₂ CH ₂ -	
109	H	4'C ₆ H ₁₁	S	-S-C ₆ H ₅	-CH ₂ CH ₂ OC ₂ H ₅	H		-COCH=CH ₂
110	H	4'-SC ₂ H ₅	S	SO ₂ C ₆ H ₅	-CH ₂ C(CH ₃) ₂ CH ₂ OH	H		

TABLE VIII
Anthrapyridone Colorants of Formula XIX

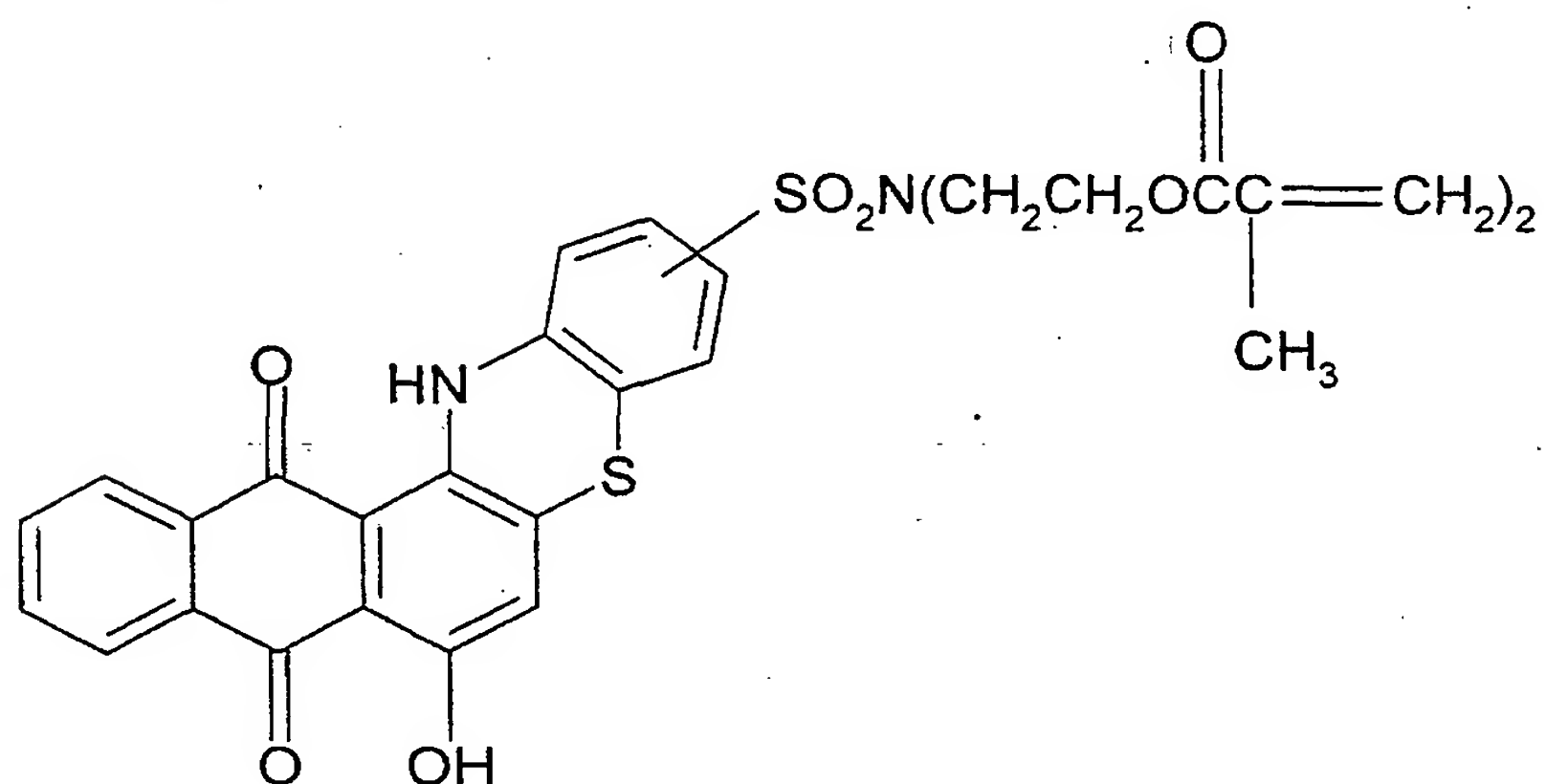


Example No.	R ₁₅	R ₁₆	X	R ₁₉	R ₂₁	R ₁	R ₂	Q
111	H	4'-CH ₃	NH	-CN	-N(CH ₃) ₂	-CH ₂ CH ₂ O-COCH=CH ₂	-CH ₂ CH ₂ -	-COCH=CH ₂
112	H	4'-CH ₃	NH	-CN	-N(C ₂ H ₅) ₂	-CH ₂ CH ₂ O-COC(CH ₃)=CH ₂	-CH ₂ CH ₂ -	-COC(CH ₃)=CH ₂
113	H	2'-OCH ₃	NH	-CN		H	-CH ₂ CH ₂ -	-COCH=CH-CH ₃

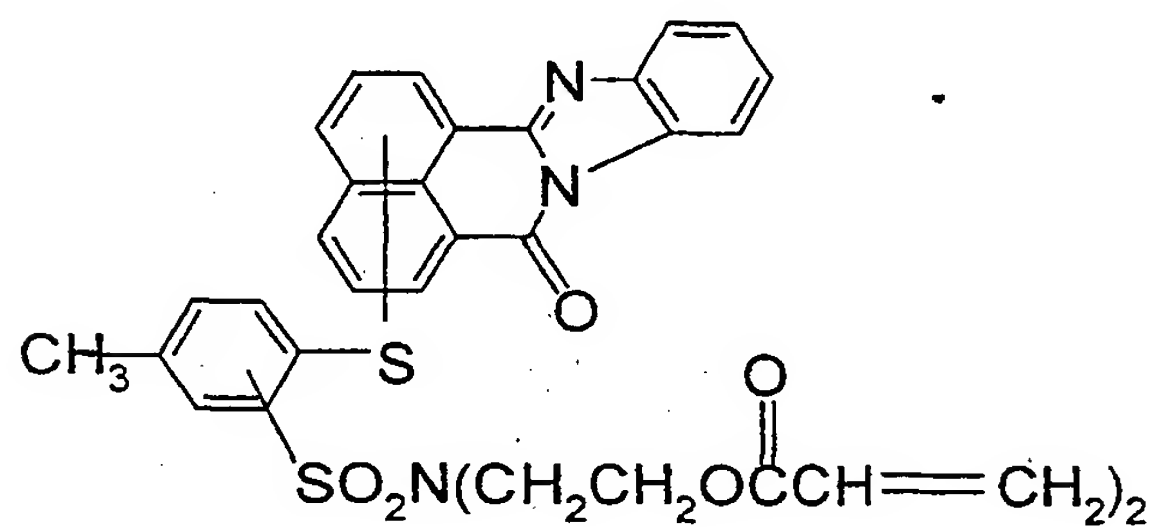
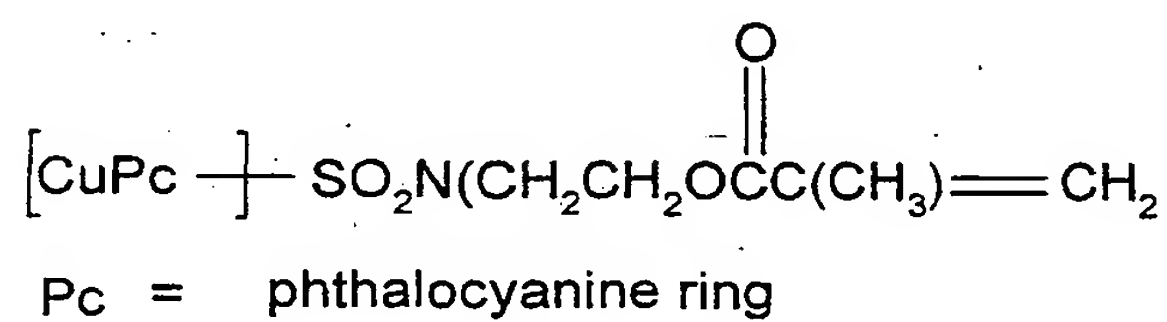
Example No.	R ₁₅	R ₁₆	X	R ₁₉	R ₂₁	R ₁	R ₂	Q
114	H	2'-OCH ₃	NH	-CN		-CH ₃	-CH ₂ CH ₂ -	
115	H	2'-OCH ₃	S	-CN	-N(CH ₃)C ₆ H ₅	-CH ₂ CH ₃	-CH ₂ CH ₂ -	-COCH=CH ₂
116	H	4'-C ₂ H ₅	S	-CN	-N(CH ₃)C ₆ H ₁₁	H	-CH ₂ CH ₂ - OCH ₂ CH ₂ -	-COC(CH ₃)=CH ₂
117	-Br	4'-C ₆ H ₁₁	S	H	H	H	-CH ₂ CH ₂ - (OCH ₂ CH ₂) ₂ -	-OCH=CH-C ₆ H ₅
118	-OC ₆ H ₅	4'-OCH ₃	S	-CN	-N(CH ₃)C ₂ H ₅	H	-	-COCH=CH-CO ₂ C ₂ H ₅
119	-SC ₆ H ₅	4'-OCH ₃	NH	-C ₆ H ₅	-CH ₃	-C ₆ H ₅	-CH ₂ CH ₂ -	
120	-SO ₂ C ₆ H ₅	4'-OCH ₃	NH	-CN	-N(C ₄ H _{9-n}) ₂	H	-CH ₂ CH ₂ - (OCH ₂ CH ₂) ₃ -	-COC(CH ₃)=CH ₂

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Table IX

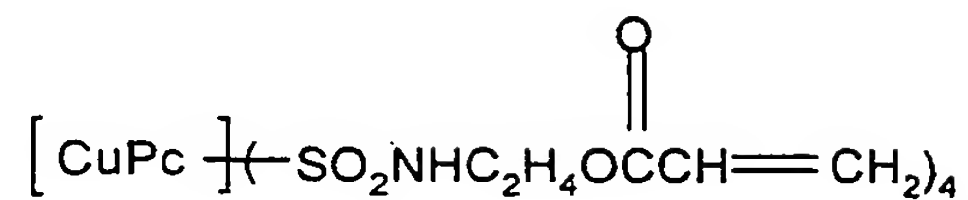
Colorants Having Miscellaneous StructuresEXAMPLE 121

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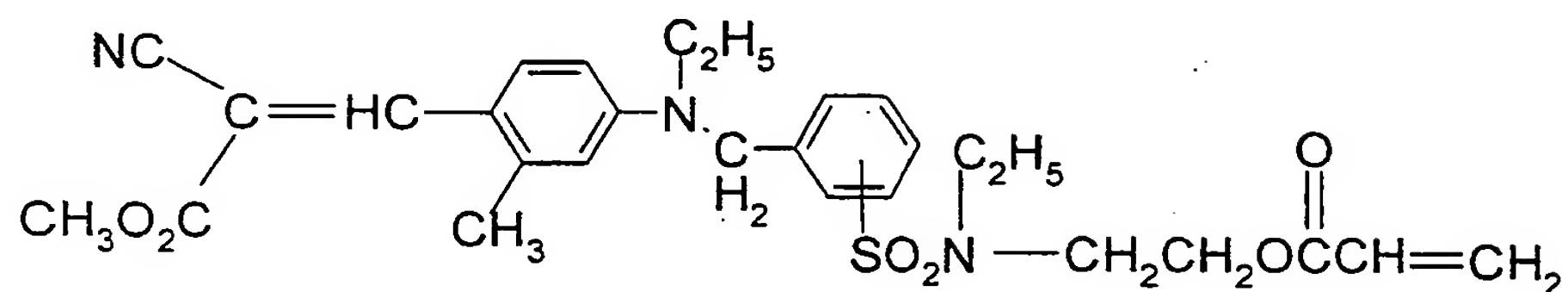
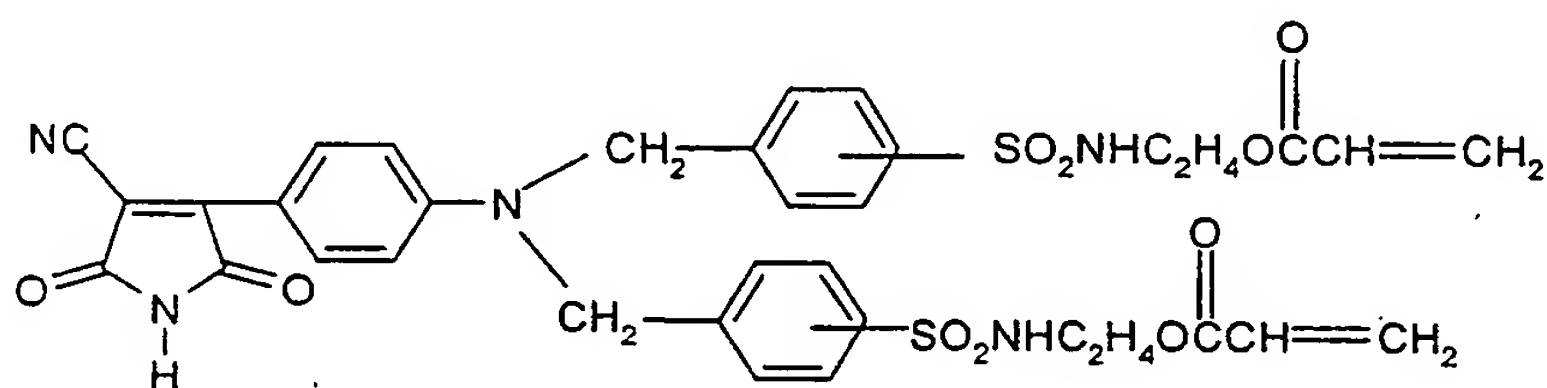
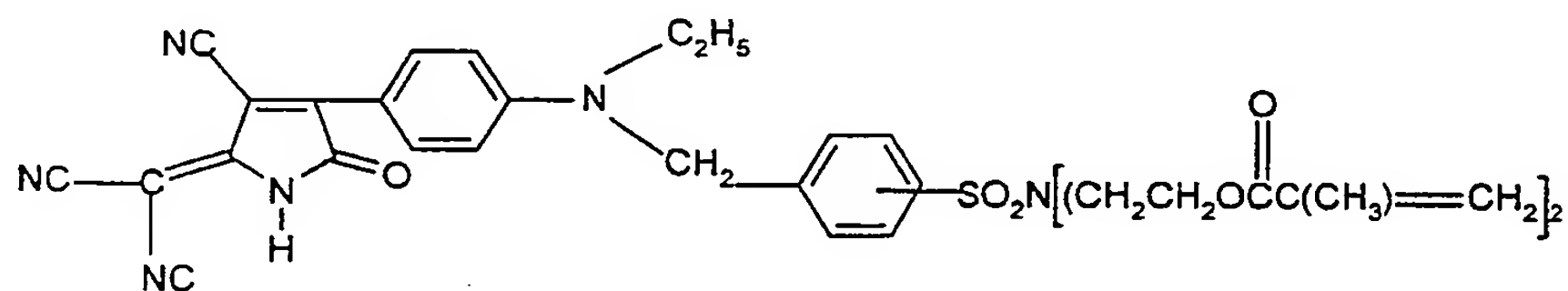
EXAMPLE 122EXAMPLE 123

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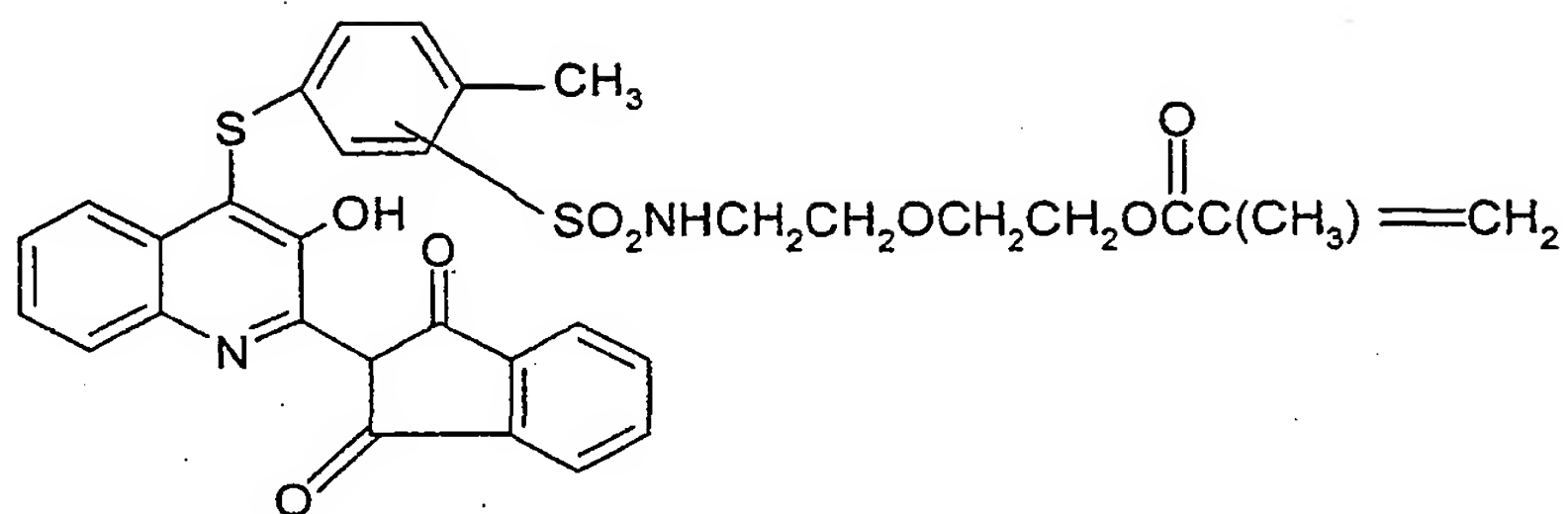
EXAMPLE 124

Pc = phthalocyanine ring

5 EXAMPLE 125EXAMPLE 126EXAMPLE 127

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EXAMPLE 128

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The thermally-stable, colored, photopolymerizable compounds which contain vinyl or substituted vinyl groups are polymerizable or copolymerizable, preferably by free radical mechanisms, said free radicals being generated by exposure to UV light by methods known in the art of preparing UV-cured resins.

5 Polymerization can be facilitated by the addition of photoinitiators. The colored polymeric materials normally are prepared by dissolving the functionalized colorants containing copolymerizable groups in a polymerizable vinyl monomer with or without another solvent and then combining with an oligomeric or polymeric material which contains one or more vinyl or substituted vinyl groups.

10 The second embodiment of the present invention is a coating composition comprising (i) one or more polymerizable vinyl compounds, i.e., vinyl compounds which are copolymerizable with the dye compounds described herein, (ii) one or more of the dye compounds described above, and (iii) at least one photoinitiator. The polymerizable vinyl compounds useful in the present invention contain at least
15 one unsaturated group capable of undergoing polymerization upon exposure to UV radiation in the presence of a photoinitiator, i.e., the coating compositions are radiation-curable. Examples of such polymerizable vinyl compounds include acrylic acid, methacrylic acid and their anhydrides; crotonic acid; itaconic acid and its anhydride; cyanoacrylic acid and its esters; esters of acrylic and methacrylic
20 acids such as allyl, methyl, ethyl, n-propyl, isopropyl, butyl, tetrahydrofurfuryl, cyclohexyl, isobornyl, n-hexyl, n-octyl, isooctyl, 2-ethylhexyl, lauryl, stearyl, and benzyl acrylate and methacrylate; and diacrylate and dimethacrylate esters of ethylene and propylene glycols, 1,3-butylene glycol, 1,4-butanediol, diethylene and dipropylene glycols, triethylene and tripropylene glycols, 1,6-hexanediol, neopentyl
25 glycol, polyethylene glycol, and polypropylene glycol, ethoxylated bisphenol A, ethoxylated and propoxylated neopentyl glycol; triacrylate and trimethacrylate esters of tris-(2-hydroxyethyl)isocyanurate, trimethylolpropane, ethoxylated and propoxylated trimethylolpropane, pentaerythritol, glycerol, ethoxylated and propoxylated glycerol; tetraacrylate and tetramethacrylate esters of pentaerythritol
30 and ethoxylated and propoxylated pentaerythritol; acrylonitrile; vinyl acetate; vinyl

toluene; styrene; N-vinyl pyrrolidinone; alpha-methylstyrene; maleate/fumarate esters; maleic/fumaric acid; crotonate esters, and crotonic acid.

5 The polymerizable vinyl compounds useful in the present invention include polymers which contain unsaturated groups capable of undergoing polymerization upon exposure to UV radiation in the presence of a photoinitiator. The preparation and application of these polymerizable vinyl compounds are well known to those skilled in the art as described, for example, in *Chemistry and Technology of UV and EB Formulation for Coatings, Inks, and Paints*, Volume II: Prepolymers and Reactive Diluents, G. Webster, editor, John Wiley and Sons, London, 1997.

10 Examples of such polymeric, polymerizable vinyl compounds include acrylated and methacrylated polyesters, acrylated and methacrylated polyethers, acrylated and methacrylated epoxy polymers, acrylated or methacrylated urethanes, acrylated or methacrylated polyacrylates (polymethacrylates), and unsaturated polyesters. The acrylated or methacrylated polymers and oligomers typically are
15 combined with monomers which contain one or more acrylate or methacrylate groups, e.g., monomeric acrylate and methacrylate esters, and serve as reactive diluents. The unsaturated polyesters, which are prepared by standard polycondensation techniques known in the art, are most often combined with either styrene or other monomers, which contain one or more acrylate or methacrylate
20 groups and serve as reactive diluents. A second embodiment for the utilization of unsaturated polyesters that is known to the art involves the combination of the unsaturated polyester with monomers that contain two or more vinyl ether groups or two or more vinyl ester groups (WO 96/01283, WO 97/48744, and EP 0 322 808).

25 The coating compositions of the present invention optionally may contain one or more added organic solvents if desired to facilitate application and coating of the compositions onto the surface of substrates. Typical examples of suitable solvents include, but are not limited to ketones, alcohols, esters, chlorinated hydrocarbons, glycol ethers, glycol esters, and mixtures thereof. Specific examples
30 include, but are not limited to acetone, 2-butanone, 2-pentanone, ethyl acetate,

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propyl acetate, isopropyl acetate, butyl acetate, isobutyl acetate, ethylene glycol diacetate, ethyl 3-ethoxypropionate, methyl alcohol, ethyl alcohol, propyl alcohol, isopropyl alcohol, butyl alcohol, ethylene glycol, propylene glycol, ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, ethylene glycol monopropyl ether, ethylene glycol monobutyl glycol, diethylene glycol monomethyl ether, diethylene glycol monoethyl ether, diethylene glycol monobutyl ether, propylene glycol monomethyl ether, diethylene glycol monobutyl ether acetate, diethylene glycol monoethyl ether acetate, ethylene glycol monobutyl ether acetate, propylene glycol monomethyl ether acetate, methylene chloride, chloroform, and mixtures thereof. The amount of added or extraneous solvent which may be present in our novel coating compositions may be in the range of 1 to 70 weight percent, more typically 1 to 25 weight percent, based on the total weight of the coating composition.

Certain polymerizable vinyl monomers may serve as both reactant and solvent. These contain at least one unsaturated group capable of undergoing polymerization upon exposure to UV radiation in the presence of a photoinitiator. Specific examples include, but are not limited to: methacrylic acid, acrylic acid, ethyl acrylate and methacrylate, methyl acrylate and methacrylate, hydroxyethyl acrylate and methacrylate, diethylene glycol diacrylate, trimethylolpropane triacrylate, 1,6 hexanediol di(meth)acrylate, neopentyl glycol diacrylate and methacrylate, vinyl ethers, divinyl ethers such as diethyleneglycol divinyl ether, 1,6-hexanediol divinyl ether, cyclohexanedimethanol divinyl ether, 1,4-butanediol divinyl ether, triethyleneglycol divinyl ether, trimethylolpropane divinyl ether, and neopentyl glycol divinyl ether, vinyl esters, divinyl esters such as divinyl adipate, divinyl succinate, divinyl glutarate, divinyl 1,4-cyclohexanedicarboxylate, divinyl 1,3-cyclohexanedicarboxylate, divinyl isophthalate, and divinyl terephthalate, N-vinyl pyrrolidone, and mixtures thereof.

In addition, the compositions of the present invention may be dispersed in water rather than dissolved in a solvent to facilitate application and coating of the substrate surface. In the water-dispersed compositions of the present invention a

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co-solvent is optionally used. Typical examples of suitable cosolvents include but are not limited to acetone, 2-butanone, methanol, ethanol, isopropyl alcohol, ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, ethylene glycol monopropyl ether, and ethylene glycol monobutyl ether, ethylene glycol, and propylene glycol. Typical examples of water-soluble ethylenically unsaturated solvents include but are not limited to: methacrylic acid, acrylic acid, N-vinyl pyrrolidone, 2-ethoxyethyl acrylate and methacrylate, polyethylene glycol dimethacrylate, polypropylene glycol monoacrylate and monomethacrylate, and mixtures thereof. The amount of suitable aqueous organic solvent (i.e., organic solvent and water) in the dispersed coating compositions of the present invention is 10 to 90 weight percent, preferably 75 to 90 weight percent of the total coating composition.

The coating compositions of the present invention contain one or more of the thermally-stable, colored, photopolymerizable compounds described herein. The concentration of the colored compound or compounds may be from 0.005 to 30.0, preferably from 0.05 to 15.0, weight percent based on the weight of the polymerizable vinyl compound(s) present in the coating composition, i.e., component (i) of the coating compositions. The coating compositions of the present invention normally contain a photoinitiator. The amount of photoinitiator typically is 1 to 15 weight percent, preferably 3 to 5 weight percent, based on the weight of the polymerizable vinyl compound(s) present in the coating composition. Typical photoinitiators include benzoin and benzoin ethers such as marketed under the tradenames ESACURE BO, EB1, EB3, and EB4 from Fratelli Lamberti; VICURE 10 and 30 from Stauffer; benzil ketals such as 2,2-dimethoxy-1,2-diphenylethan-1-one (IRGACURE 651), 2-hydroxy-2-methyl-1-phenylpropan-1-one (IRGACURE 1173), 2-methyl-2-morpholino-1-(p-methylthiophenyl)propan-1-one (IRGACURE 907), alpha-hydroxyalkylphenones such as (1-hydroxycyclohexyl)(phenyl)methanone (IRGACURE 184), 2-benzyl-2-(dimethylamino)-1-(4-morpholinophenyl)butan-1-one (IRGACURE 369), 2-hydroxy-2-methyl-1-phenylpropan-1-one (IRGACURE 1173) from Ciba Geigy,

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Uvatone 8302 by Upjohn; alpha, alpha-dialkoxyacetophenone derivatives such as DEAP and UVATONE 8301 from Upjohn; DAROCUR 116, 1173, and 2959 by Merck; and mixtures of benzophenone and tertiary amines. In pigmented coating compositions, the rate of cure can be improved by the addition of a variety of phosphine oxide photoinitiators such as bis(2,4,6-trimethylbenzoyl)-phenylphosphine oxide (Irganox 819), Irgacure 819, 1700, and 1700 and phosphine oxide mixtures such as a 50/50 by weight mixtures of IRGACURE 1173 and 2,4,6-trimethylbenzoyldiphenylphosphine oxide (DAROCUR 4265) from Ciba. Further details regarding such photoinitiators and curing procedures may be found in the published literature such as U.S. Patent 5,109,097, incorporated herein by reference. Depending upon the thickness of the coating (film), product formulation, photoinitiator type, radiation flux, and source of radiation, exposure times to ultraviolet radiation of 0.5 second to 30 minutes (50-5000 mJ/square cm) typically are required for curing. Curing also can occur from solar radiation, i.e., sunshine.

The coating compositions of the present invention may contain one or more additional components typically present in coating compositions. Examples of such additional components include leveling, rheology, and flow control agents such as silicones, fluorocarbons or cellulose; flattening agents; pigment wetting and dispersing agents; surfactants; ultraviolet (UV) absorbers; UV light stabilizers; tinting pigments; defoaming and antifoaming agents; anti-settling, anti-sag and bodying agents; anti-skinning agents; anti-flooding and anti-floating agents; fungicides and mildewcides; corrosion inhibitors; thickening agents; and/or coalescing agents. The coating compositions of the present invention also may contain non-reactive modifying resins. Typical non-reactive modifying resins include homopolymers and copolymers of acrylic and methacrylic acid; homopolymers and copolymers of alkyl esters of acrylic and methacrylic acid such as methyl, ethyl, n-propyl, isopropyl, butyl, tetrahydrofurfuryl, cyclohexyl, isobornyl, n-hexyl, n-octyl, isooctyl, 2-ethylhexyl, lauryl, stearyl, and benzyl acrylate and methacrylate; acrylated and methacrylated urethane, epoxy, and

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polyester resins, silicone acrylates, cellulose esters such as cellulose acetate butyrates, cellulose acetate, propionates, nitrocellulose, cellulose ethers such as methyl cellulose, ethyl cellulose, hydroxypropyl cellulose, and hydroxypropyl methyl cellulose.

5 Typical plasticizers include alkyl esters of phthalic acid such as dimethyl phthalate, diethyl phthalate, dipropyl phthalate, dibutyl phthalate, and dioctyl phthalate; citrate esters such as triethyl citrate and tributyl citrate; triacetin and tripropionin; and glycerol monoesters such as Eastman 18-04, 18-07, 18-92 and 18-
10 can be found in *Raw Materials Index*, published by the National Paint & Coatings Association, 1500 Rhode Island Avenue, N.W., Washington, D.C. 20005.

 The third embodiment of the present invention pertains to a polymeric composition, typically a polymeric coating, comprising a polymer of one or more acrylic acid esters, one or more methacrylic acid esters and/or other polymerizable
15 vinyl compounds, having copolymerized therein one or more of the thermally-stable, colored, photopolymerizable compounds described herein. The colored polymeric compositions provided by our invention may be prepared from the coating compositions described above and typically contain from 0.005 to 30.0 weight percent, preferably from 0.5 to 15.0 weight percent, of the reactive or
20 polymerized residue of one or more of the vinyl dye compounds described herein based on the weight of the composition or coating. The novel polymeric coatings may have a thickness of 2.5 to 150 microns, more typically 15 to 65 microns.

 The polymeric coatings of the present invention typically have a solvent resistance of at least 100 MEK double rubs using ASTM Procedure D-3732;
25 preferably a solvent resistance of at least 200 double rubs. Such coatings also typically have a pencil hardness of greater than or equal to F using ASTM Procedure D-3363; preferably a pencil hardness of greater than or equal to H. The coating compositions can be applied to substrates with conventional coating equipment. The coated substrates are then exposed to radiation such as ultraviolet
30 light in air or in nitrogen which gives a cured finish. Mercury vapor or Xenon

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lamps are applicable for the curing process. The coatings of the present invention can also be cured by electron beam.

5 The radiation-curable coating compositions of this invention are suitable as adhesives and coatings for such substrates as metals such as aluminum and steel, plastics, glass, wood, paper, and leather. On wood substrates the coating compositions may provide both overall transparent color and grain definition. Various aesthetically-appealing effects can be achieved thereby. Due to reduced grain raising and higher film thicknesses, the number of necessary sanding steps in producing a finished wood coating may be reduced when using the colored coating compositions of the invention rather than conventional stains. Coating compositions within the scope of our invention may be applied to automotive base coats where they can provide various aesthetically-appealing effects in combination with the base coats and color differences dependent on viewing angle (lower angles create longer path lengths and thus higher observed color intensities). This may provide similar styling effects as currently are achieved with metal flake orientation in base coats.

15 Various additional pigments, plasticizers, and stabilizers may be incorporated to obtain certain desired characteristics in the finished products. These are included in the scope of the invention.

20

Coating, Curing, and Testing Procedures:

Samples of formulations were used to coat glass plates using a knife blade. The wet film thickness was about 15 to 75 microns (0.6 to 3.0 mils). The solvent was evaporated to give a clear, somewhat tacky film. Prior to exposure to UV radiation, each film was readily soluble in organic solvents.

25

The dried film on the glass plate was exposed to UV radiation from a 200 watt per inch medium pressure mercury vapor lamp housed in an American Ultraviolet Company instrument using a belt speed of 25 ft. per minute. One to five passes under the lamp resulted in a crosslinked coating with maximum hardness and solvent resistance.

30

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Each cured coating (film) may be evaluated for Konig Pendulum Hardness (ASTM D4366 DIN 1522), solvent resistance by the methyl ethyl ketone double-rub test, and solubility in acetone before and after exposure to UV radiation. The damping time for Konig Pendulum Hardness on uncoated glass is 250 seconds; coatings with hardness above 100 seconds are generally considered hard coatings. The methyl ethyl ketone (MEK) double rub test is carried out in accordance with ASTM Procedure D-3732 by saturating a piece of cheese cloth with methyl ethyl ketone, and with moderate pressure, rubbing the coating back and forth. The number of double rubs is counted until the coating is removed. The acetone solubility test is carried out by immersing a dry, pre-weighed sample of the cured film in acetone for 48 hours at 25°C. The film is removed, dried for 16 hours at 60°C in a forced-air oven, and reweighed. The weight percent of the insoluble film remaining is calculated from the data.

15 Coating Examples

The coatings and coating compositions provided by the present invention and the preparation thereof are further illustrated by the following examples.

20 EXAMPLE 129

A colored, photopolymerizable composition was prepared by thoroughly mixing 22.9 g of dipropylene glycol diacrylate, 69.1 g of Jaegalux UV-1500 (acrylated polyester oligomers), the blue compound of Example 6b (4 g of a 1.25% solution of the colored compound in dipropylene glycol diacrylate), and 4 g of Darocure 1173 photoinitiator in a small Cowles mixer until the components were completely dispersed. This coating composition was drawn down with a wire wound rod to provide a 25.4 micron (1 mil) thick coating on an Oak wood panel. This panel was passed through a UV cure machine at a speed of 6.1 meters per minute (20 feet/minute) using a lamp with an intensity of 118.1 watts per cm (300 watts per inch). Hardness measurements were conducted on glass using a Konig pendulum and did not indicate any significant loss of hardness due to incorporation

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of the dye; hardness was 83 Konig seconds. Adhesion of the coating to an oak wood panel was measured using the crosshatch adhesion method according to ASTM method D 3359 (ISO 2409). A right angle lattice pattern (6 lines in each direction) is cut into the coating, penetrating to the substrate, creating 25 squares with each side of the squares measuring 1 mm. A 2.5 cm (1 inch) wide piece of tape is applied to the lattice, pressure is applied, and then the tape is pulled from the substrate. If the edges are smooth and none of the squares are detached, the adhesion is 100 % (ASTM rating 5B). On the wood panel a 5B rating was achieved for both the reference and the dye-containing coatings. All the coatings withstood more than 300 MEK double rubs. No loss of solvent resistance was observed with incorporation of the dye.

EXAMPLE 130

A colored, photopolymerizable composition was prepared by thoroughly mixing 10.0 g dipropylene glycol diacrylate, 10.0 g tripropylene glycol triacrylate, 20.0 g Jaegalux UV-1500 (acrylated polyester oligomers), 15 g Jaegalux UV-3800 (acrylated epoxy oligomers), the blue compound of Example 6b (5.5 g of a 1.25 % solution of the dye in dipropylene glycol diacrylate), and 2.2 gram of Irgacure 819 photoinitiator in a small Cowles mixer until the components were completely dispersed (20 minutes at 12,000 revolutions per minute). This coating composition was drawn down with a wire wound rod to provide a 38.1 micron (1.5 mil) thick coating on a cold rolled steel panel (iron phosphate pretreatment) and on polyethylene terephthalate sheet. The coated steel panel and polyester sheet were passed through a UV cure machine at a speed of 6.1 meters per minute (20 feet/minute) using a lamp with an intensity of 118.1 watts per cm (300 watts per inch). The Konig pendulum hardness of the coatings on the steel panels was 126 Konig seconds. No significant loss of hardness (relative to the reference coating) due to incorporation of the dye was observed. All the coatings withstood more than 500 MEK double rubs. No significant loss of solvent resistance was observed with incorporation of the dye. Adhesion tests of the coatings on polyethylene

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terephthalate sheeting using the crosshatch adhesion method described in Example 129 showed no loss of adhesion due to incorporation of the dye and 100% adhesion for the coatings.

5 EXAMPLE 131

 A colored, photopolymerizable composition was prepared by thoroughly mixing the blue compound of Example 6b (10 g of a 2% solution of the dye in dipropylene glycol diacrylate), 20 gram trimethylol propane triacrylate, 20 g of polyester acrylate oligomer, 15 g of bisphenol A epoxy acrylate, and 4 gram of PI 1173 photoinitiator in a small Cowles mixer until the components were completely dispersed. The resulting coating composition was drawn down with a wire wound rod to provide a 25.4 micron (1 mil) thick coating on a 20 gauge sheet (1.27 mm - 50 mils - thick) of polyethylene terephthalate (PET). The coated sheet was passed through a UV cure machine at a speed of 6.1 meters per minute (20 feet/minute) using a lamp with an intensity of 118.1 watts per cm (300 watts per inch). Hardness measured on glass by the Konig Pendulum method indicated no reduction of the hardness due to the dye; hardness was 105 Konig seconds. Adhesion tests of the coatings on polyethylene terephthalate sheet in accordance with the crosshatch adhesion method described in Example 129 showed no loss of adhesion due to incorporation of the dye and 100% adhesion for the coatings. All the coatings withstood more than 300 MEK double rubs. No significant loss of solvent resistance was observed with incorporation of the dye. The coating provided an attractive even color over the entire coated sheet.

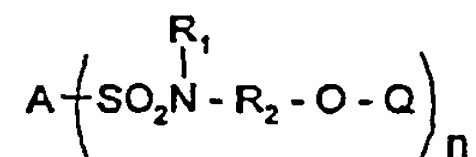
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CLAIMS

We claim:

1. A photopolymerizable colorant compound having the formula:



5

I

wherein

A is a mono-, di-, tri- or tetravalent chromophore;

R₁ is selected from hydrogen, C₁ - C₆ alkyl, substituted C₁ - C₆ alkyl, C₃ - C₈ cycloalkyl, aryl and -R₂-OQ;

10

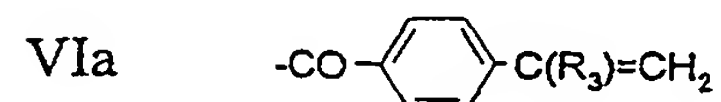
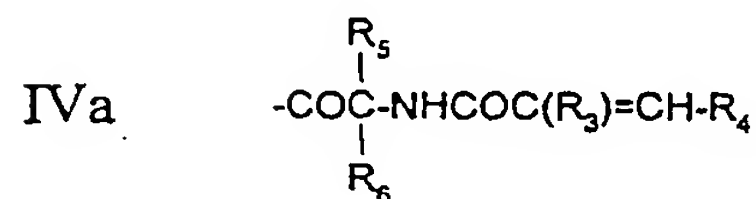
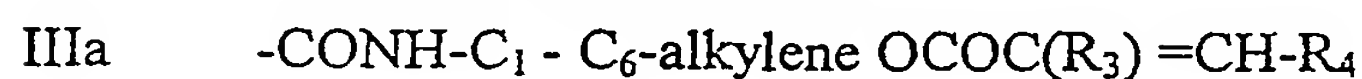
R₂ is selected from C₂ - C₈ alkylene, arylene, C₃ - C₈ cycloalkylene, arylene - C₁ - C₆ alkylene, arylene-oxy-C₁ - C₆ alkylene, arylene-thio - C₁ - C₆ alkylene, 1,4-cyclohexylenedimethylene and $(-\text{CH}_2\text{CH}_2\text{O})_m-\text{CH}_2\text{CH}_2-$;

m is 1-3;

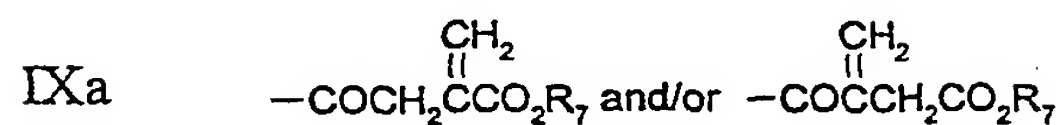
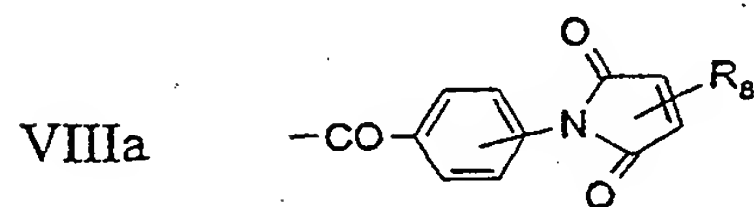
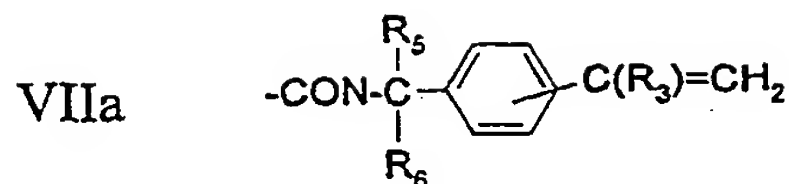
n is 1-4;

15

Q is an ethylenically-unsaturated, photopolymerizable group selected from the following organic radicals:



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wherein

R_3 is selected from hydrogen or $C_1 - C_6$ alkyl;

R_4 is selected from hydrogen, $C_1 - C_6$ alkyl;

phenyl; phenyl substituted with one or more groups selected from $C_1 - C_6$ alkyl,

- 5 $C_1 - C_6$ alkoxy, $-N(C_1 - C_6 \text{ alkyl})_2$, nitro, cyano, $C_2 - C_6$ alkoxycarbonyl, $C_2 - C_6$ alkanoyloxy and halogen; 1- and 2-naphthyl; 1- and 2-naphthyl substituted with $C_1 - C_6$ alkyl and $C_1 - C_6$ alkoxy; 2- and 3-thienyl; 2- and 3-thienyl substituted with $C_1 - C_6$ alkyl or halogen; 2- and 3-furyl; 2- and 3-furyl substituted with $C_1 - C_6$ alkyl;

- 10 R_5 and R_6 are independently selected from hydrogen, $C_1 - C_6$ alkyl, substituted $C_1 - C_6$ alkyl, aryl or may be combined to represent a $-(-CH_2-)-_{3-5}$ radical;

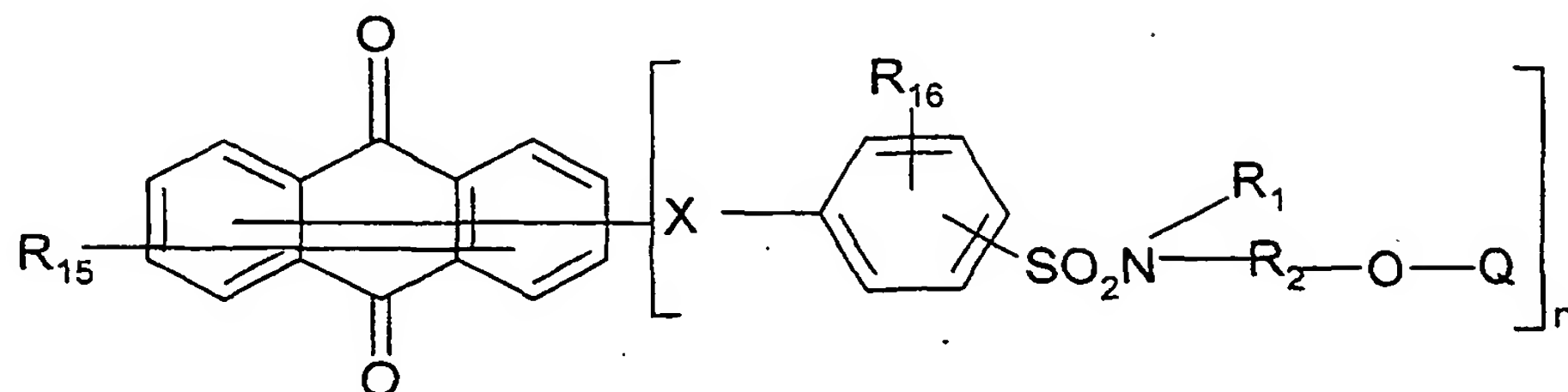
R_7 is hydrogen or a group selected from $C_1 - C_6$ alkyl, substituted $C_1 - C_6$ alkyl, $C_3 - C_8$ alkenyl, $C_3 - C_8$ cycloalkyl and aryl;

- 15 R_8 is selected from hydrogen, $C_1 - C_6$ alkyl and aryl.

2. A photopolymerizable colorant according to Claim 1 wherein A is a mono-, di-, tri- or tetravalent chromophore selected from residues of anthraquinone, anthrapyridone, anthrapyrizidine, anthrapyrizidine, anthrapyrizole, anthraiso-thiazole, 14H-naphtho[2,3-a]-phenothiazine-8,13-dione, phthalocyanine, metal phthalocyanine, methine, bis-methine, perinone, coumarin, quinophthalone, 3-aryl-2,5-dioxypyrroline, and 3-aryl-5-dicyanomethylene-2-oxypyrroline.
- 20

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3. A photopolymerizable colorant according to Claim 1 having the formula



5 wherein

R_1 is selected from hydrogen, $C_1 - C_6$ alkyl, substituted $C_1 - C_6$ alkyl, $C_3 - C_8$ cycloalkyl, aryl and $-R_2-OQ$;

R_2 is selected from $C_2 - C_8$ alkylene, arylene, $C_3 - C_8$ cycloalkylene, arylene
- $C_1 - C_6$ alkylene, arylene-oxy- $C_1 - C_6$ alkylene, arylene-thio- $C_1 - C_6$ alkylene,
10 1,4-cyclohexylenedimethylene and $-(CH_2CH_2O)_m-CH_2CH_2-$;

m is 1-3;

n is 1-4;

R_{15} is hydrogen or R_{15} represents 1-4 groups selected from amino; C_1-C_8 -
alkylamino; C_1-C_8 -alkylamino substituted with one or more groups selected from
15 hydroxy, cyano, halogen, aryl, heteroaryl, C_3-C_8 -cycloalkyl, furyl, C_1-C_6 -alkoxy,
 C_1-C_6 -alkylthio, arylthio, aryloxy and $-OCH_2CH_2O(OCH_2CH_2)_{1-3}OR'$, wherein R' is
selected from hydrogen, C_1-C_6 -alkyl and C_2-C_6 -alkanoyloxy; C_3-C_8 -cycloalkyl-
amino; C_3-C_8 -alkenylamino; C_3-C_8 -alkynylamino; arylamino; furfurylamino;
 C_1-C_6 -alkoxy; $-OCH_2CH_2(OCH_2CH_2)_{1-3}OR'$, wherein R' is as previously defined;
20 halogen; hydroxy; C_1-C_6 -alkylthio; arylthio; aryl; aryloxy; arylsulfonyl;
 C_2-C_6 -alkanoyl; aroyl; C_2-C_6 -alkanoyloxy; C_2-C_6 -alkoxycarbonyl; heteroaryl;
heteroarylthio; cyano; nitro; trifluoromethyl; thiocyno; $-SO_2C_1-C_6$ -alkyl;
 $-SO_2NH_2$; $-SO_2NHC_1-C_6$ -alkyl; $-SO_2N(C_1-C_6\text{ alkyl})_2$; $-SO_2N(C_1-C_6\text{ alkyl})\text{aryl}$;
 $-SO_2NH\text{-aryl}$; $-CONH_2$; $-CONHC_1-C_6$ -alkyl; $-CON(C_1-C_6\text{-alkyl})_2$; $-CONH\text{-aryl}$;

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-CON(C₁-C₆alkyl) aryl; C₁-C₆ alkyl; tetrahydrofurfurylamino; -CH₂-cyclohexane-1,4-diyl-CH₂OR', wherein R' is as previously defined; or

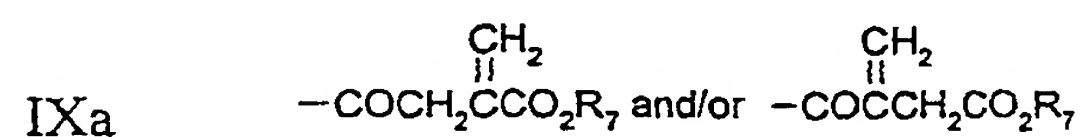
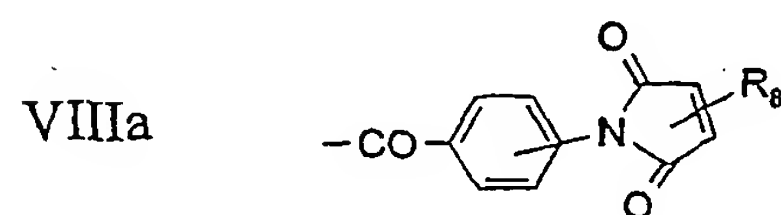
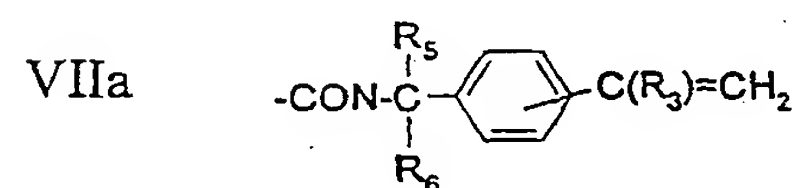
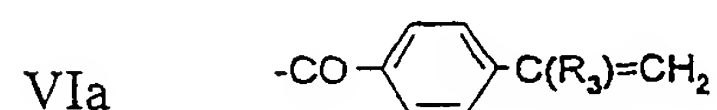
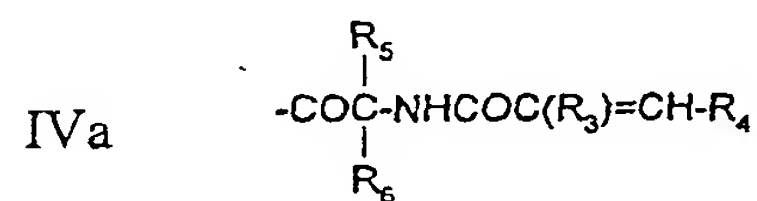


R₁₆ is hydrogen or 1-2 groups selected from C₁-C₆-alkyl, C₁-C₆-alkoxy and halogen;

5 X is a covalent bond or a linking group selected from -O-, -S-, -SO₂-, -NHCO-, -NHSO₂-, -NHCONH-, -OC₂-C₆ alkylene-, -OC₂-C₆-alkylene-O-, -S-C₂-C₆-alkylene-O-and, -O(CH₂CH₂O)₁₋₃-; and

Q is an ethylenically-unsaturated, photopolymerizable group selected from the following organic radicals:

10



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wherein

R_3 is selected from hydrogen or $C_1 - C_6$ alkyl;

R_4 is selected from hydrogen, $C_1 - C_6$ alkyl;

phenyl; phenyl substituted with one or more groups selected from $C_1 - C_6$ alkyl,

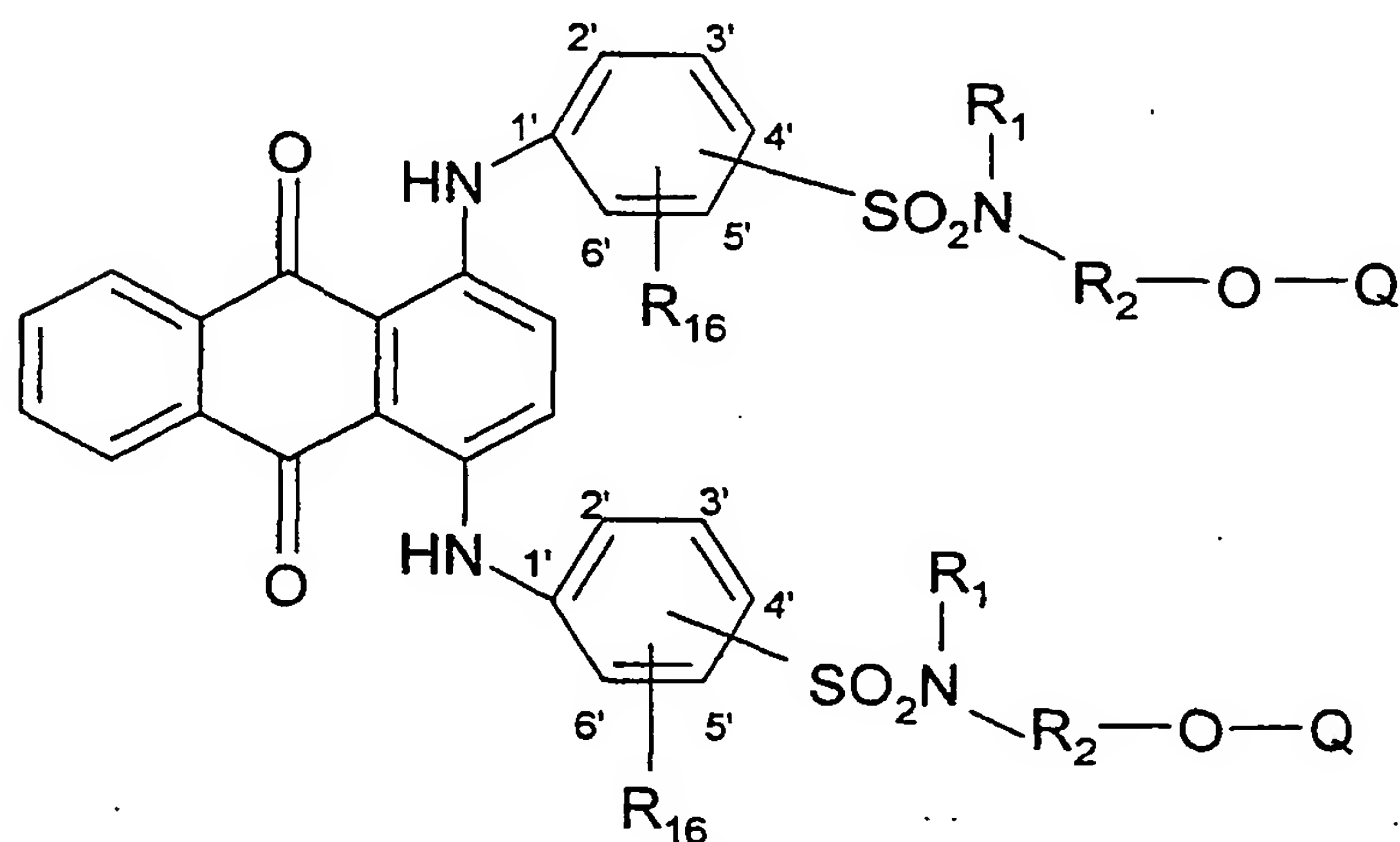
5 $C_1 - C_6$ alkoxy, $-N(C_1 - C_6 \text{ alkyl})_2$, nitro, cyano, $C_2 - C_6$ alkoxy carbonyl, $C_2 - C_6$ alkoxyloxy and halogen; 1- and 2-naphthyl; 1- and 2-naphthyl substituted with $C_1 - C_6$ alkyl and $C_1 - C_6$ alkoxy; 2- and 3-thienyl; 2- and 3-thienyl substituted with $C_1 - C_6$ alkyl or halogen; 2- and 3-furyl; 2- and 3-furyl substituted with $C_1 - C_6$ alkyl;

10 R_5 and R_6 are independently selected from hydrogen, $C_1 - C_6$ alkyl, substituted $C_1 - C_6$ alkyl, aryl or may be combined to represent a $-(-CH_2-)-_{3-5}$ radical;

R_7 is hydrogen or a group selected from $C_1 - C_6$ alkyl, substituted $C_1 - C_6$ alkyl, $C_3 - C_8$ alkenyl, $C_3 - C_8$ cycloalkyl and aryl; and

15 R_8 is selected from hydrogen, $C_1 - C_6$ alkyl and aryl.

4. A photopolymerizable colorant according to Claim 1 having the formula



XIV

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wherein

R_1 is selected from hydrogen or $C_1 - C_6$ alkyl;

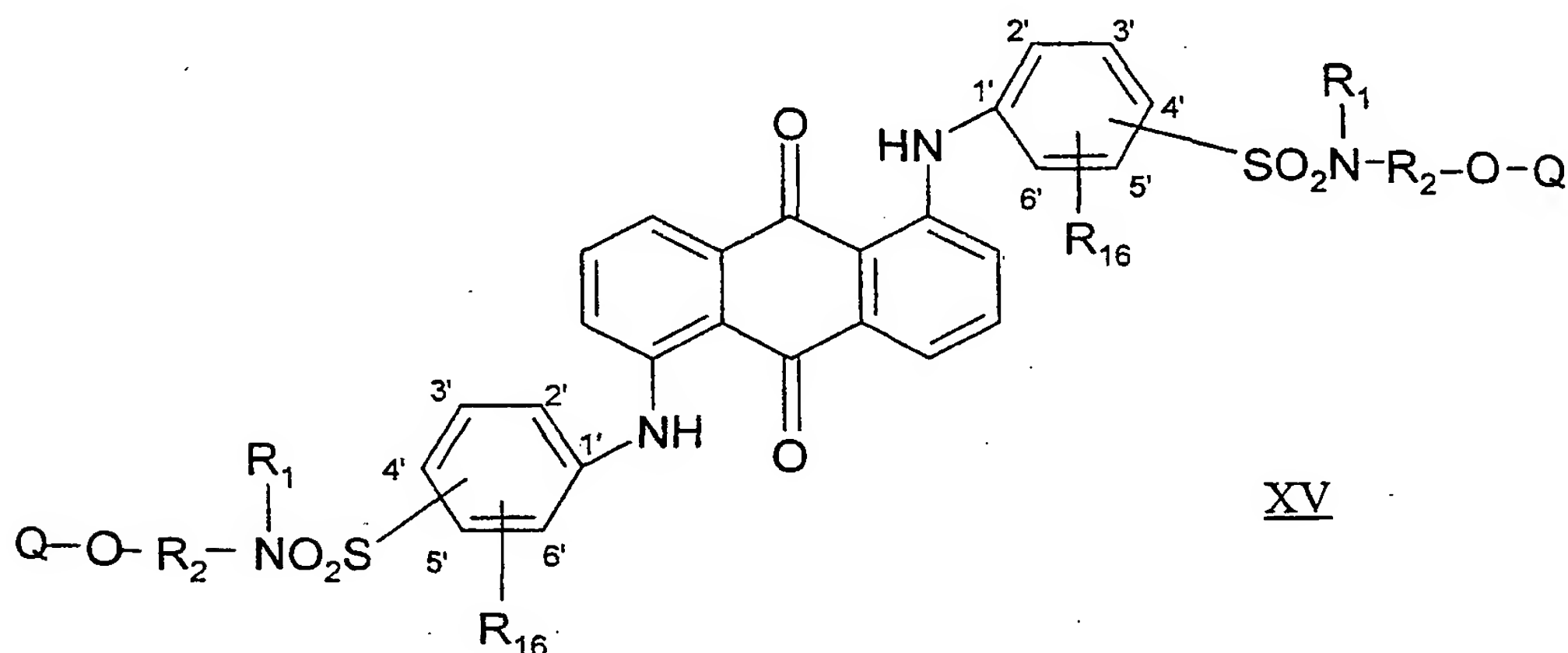
R_2 is selected from $C_2 - C_8$ alkylene, arylene, $C_3 - C_8$ cycloalkylene, arylene- $C_1 - C_6$ alkylene, arylene-oxy- $C_1 - C_6$ alkylene, arylene-thio- $C_1 - C_6$ alkylene, 1,4-cyclohexylenedimethylene and $(-CH_2CH_2O)_m-CH_2CH_2-$;

m is 1-3;

R_{16} is selected from 2',6'-di- $C_1 - C_6$ alkyl; and

Q is $-COC(R_3)=CH_2$ wherein R_3 is selected from hydrogen or methyl.

- 10 5. A photopolymerizable colorant according to Claim 1 having the formula



wherein

R_1 is selected from hydrogen or $C_1 - C_6$ alkyl;

R_2 is selected from $C_2 - C_8$ alkylene, arylene, $C_3 - C_8$ cycloalkylene, arylene- $C_1 - C_6$ alkylene, arylene-oxy- $C_1 - C_6$ alkylene, arylene-thio- $C_1 - C_6$ alkylene, 1,4-cyclohexylenedimethylene and $(-CH_2CH_2O)_m-CH_2CH_2-$;

m is 1-3;

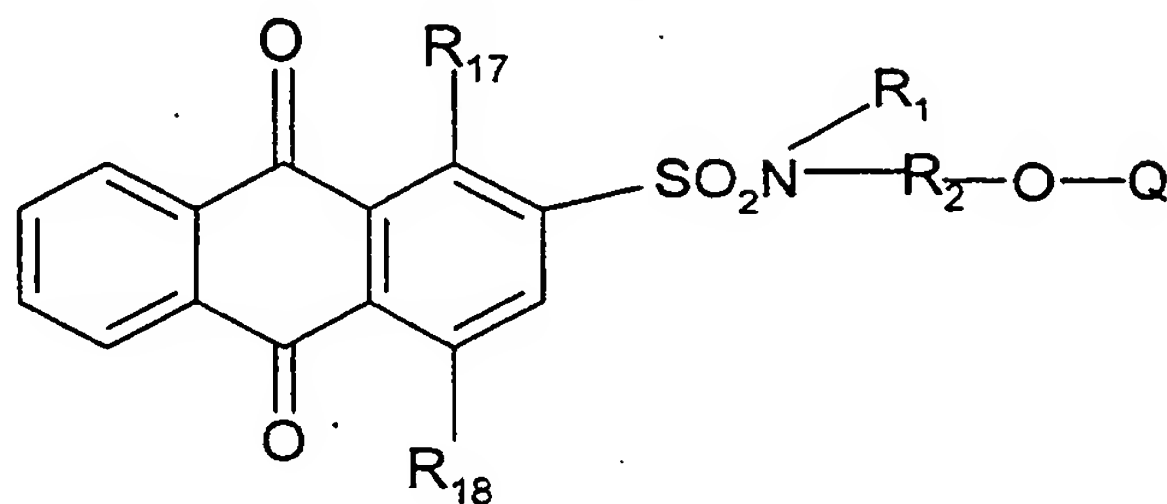
R_{16} is selected from 2',6'-di- $C_1 - C_6$ alkyl; and

Q is $-COC(R_3)=CH_2$ wherein R_3 is selected from hydrogen or methyl.

20

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6. A photopolymerizable colorant according to Claim 1 having the formula



XI

wherein

5 R_1 is selected from hydrogen, $C_1 - C_6$ alkyl, substituted $C_1 - C_6$ alkyl, $C_3 - C_8$ cycloalkyl, aryl and $-R_2-OQ$;

R_2 is selected from $C_2 - C_8$ alkylene, arylene, $C_3 - C_8$ cycloalkylene, arylene- $C_1 - C_6$ alkylene, arylene-oxy- $C_1 - C_6$ alkylene, arylene-thio- $C_1 - C_6$ alkylene, 1,4-cyclohexylenedimethylene and $-(-CH_2CH_2O)_m-CH_2CH_2-$;

m is 1-3;

10 R_{17} is selected from amino; C_1-C_8 -alkylamino, substituted C_1-C_8 -alkylamino is defined above, C_3-C_8 -cycloalkylamino, C_3-C_8 -alkenylamino, C_3-C_8 -alkynylamino and arylamino;

15 R_{18} is selected from halogen, amino, C_1-C_8 alkylamino, substituted C_1-C_8 -alkylamino, C_3-C_8 -cycloalkylamino, C_3-C_8 -alkenylamino, C_3-C_8 -alkynylamino, arylamino, hydroxy, arylthio, heteroarylthio, C_2-C_6 -alkanoylamino, aroylamino, C_1-C_6 -alkylsulfonylamino, and arylsulfonylamino; and

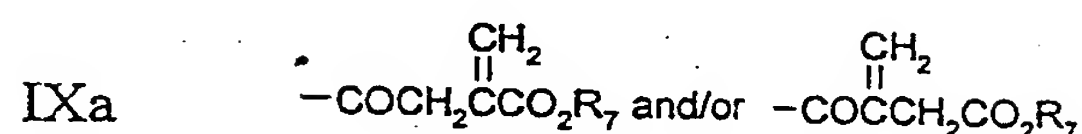
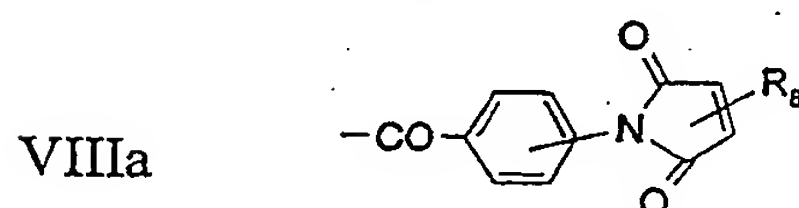
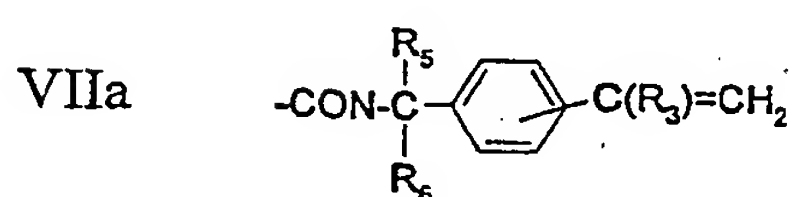
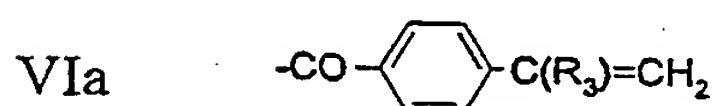
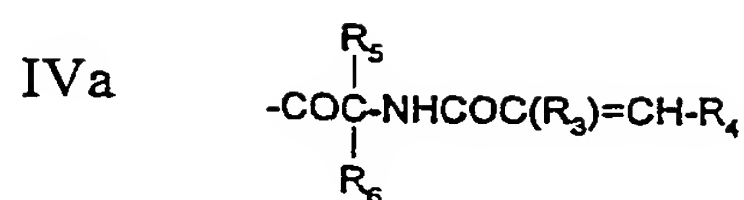
Q is an ethylenically-unsaturated, photopolymerizable group selected from the following organic radicals:

Ia $-COC(R_3)=CH-R_4$

IIa $-CONHCOC(R_3)=CH-R_4$

IIIa $-CONH-C_1 - C_6$ -alkylene $OCOC(R_3) =CH-R_4$

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wherein

R_3 is selected from hydrogen or $C_1 - C_6$ alkyl;

R_4 is selected from hydrogen, $C_1 - C_6$ alkyl;

phenyl; phenyl substituted with one or more groups selected from $C_1 - C_6$ alkyl, $C_1 - C_6$ alkoxy, $-N(C_1 - C_6 \text{ alkyl})_2$, nitro, cyano, $C_2 - C_6$ alkoxycarbonyl, $C_2 - C_6$ alkanoyloxy and halogen; 1- and 2-naphthyl; 1- and 2-naphthyl substituted with $C_1 - C_6$ alkyl and $C_1 - C_6$ alkoxy; 2- and 3-thienyl; 2- and 3-thienyl substituted with $C_1 - C_6$ alkyl or halogen; 2- and 3-furyl; 2- and 3-furyl substituted with $C_1 - C_6$ alkyl;

R_5 and R_6 are independently selected from hydrogen, $C_1 - C_6$ alkyl, substituted $C_1 - C_6$ alkyl, aryl or may be combined to represent a $-(-CH_2-)-_{3-5}$ radical;

R_7 is hydrogen or a group selected from $C_1 - C_6$ alkyl, substituted $C_1 - C_6$ alkyl, $C_3 - C_8$ alkenyl, $C_3 - C_8$ cycloalkyl and aryl; and

R_8 is selected from hydrogen, $C_1 - C_6$ alkyl and aryl.

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7. A photopolymerizable colorant according to Claim 6 wherein

R_1 is selected from hydrogen, $C_1 - C_6$ alkyl, and $-R_2-OQ$;

R_2 is selected from $C_2 - C_8$ alkylene, arylene, $C_3 - C_8$ cycloalkylene, arylene- $C_1 - C_6$ alkylene, arylene-oxy- $C_1 - C_6$ alkylene, arylene-thio- $C_1 - C_6$ alkylene, 1,4-cyclohexylenedimethylene and $-(CH_2CH_2O)_m-CH_2CH_2-$;

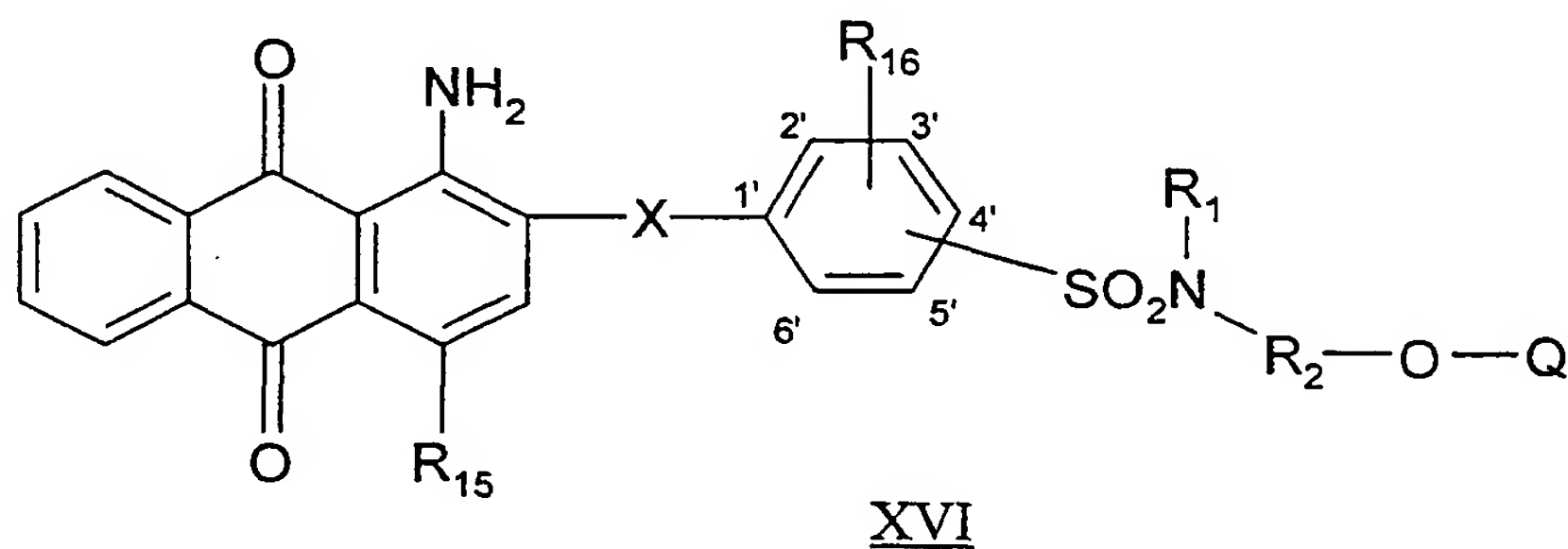
m is 1-3;

R_{17} is selected from amino; C_1-C_8 -alkylamino, substituted C_1-C_8 -alkylamino is defined above, C_3-C_8 -cycloalkylamino, C_3-C_8 -alkenylamino, C_3-C_8 -alkynylamino and arylamino;

R_{18} is selected from halogen, amino, C_1-C_8 alkylamino, substituted C_1-C_8 -alkylamino, C_3-C_8 -cycloalkylamino, C_3-C_8 -alkenylamino, C_3-C_8 -alkynylamino, arylamino, hydroxy, arylthio, heteroarylthio, C_2-C_6 -alkanoylamino, aroylamino, C_1-C_6 -alkylsulfonylamino, and arylsulfonylamino; and

Q is $-COC(R_3)=CH_2$ wherein R_3 is selected from hydrogen or methyl.

8. A photopolymerizable colorant according to Claim 1 having the formula



wherein

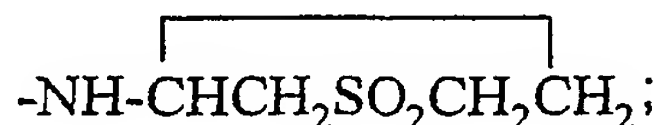
R_1 is selected from hydrogen, $C_1 - C_6$ alkyl, and $-R_2-OQ$;

R_2 is selected from $C_2 - C_8$ alkylene, arylene, $C_3 - C_8$ cycloalkylene, arylene- $C_1 - C_6$ alkylene, arylene-oxy- $C_1 - C_6$ alkylene, arylene-thio- $C_1 - C_6$ alkylene, 1,4-cyclohexylenedimethylene and $-(CH_2CH_2O)_m-CH_2CH_2-$;

m is 1-3;

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- R_{15} is selected from hydrogen, amino; C_1 - C_8 -alkylamino; C_1 - C_8 -alkylamino substituted with one or more groups selected from hydroxy, cyano, halogen, aryl, heteroaryl, C_3 - C_8 -cycloalkyl, furyl, C_1 - C_6 -alkoxy, C_1 - C_6 -alkylthio, arylthio, aryloxy and $-OCH_2CH_2O(OCH_2CH_2)_{1-3}OR'$, wherein R' is selected from hydrogen, C_1 - C_6 -alkyl and C_2 - C_6 -alkanoyloxy; C_3 - C_8 -cycloalkylamino; C_3 - C_8 -alkenylamino; C_3 - C_8 -alkynylamino; arylamino; furfurylamino; C_1 - C_6 -alkoxy; $-OCH_2CH_2-(OCH_2CH_2)_{1-3}OR'$, wherein R' is as previously defined; halogen; hydroxy; C_1 - C_6 -alkylthio; arylthio; heteroarylthio; thiocyano; tetrahydrofurfurylamino; $-CH_2$ -cyclohexane-1,4-diyl- CH_2OR' , wherein R' is as previously defined; or

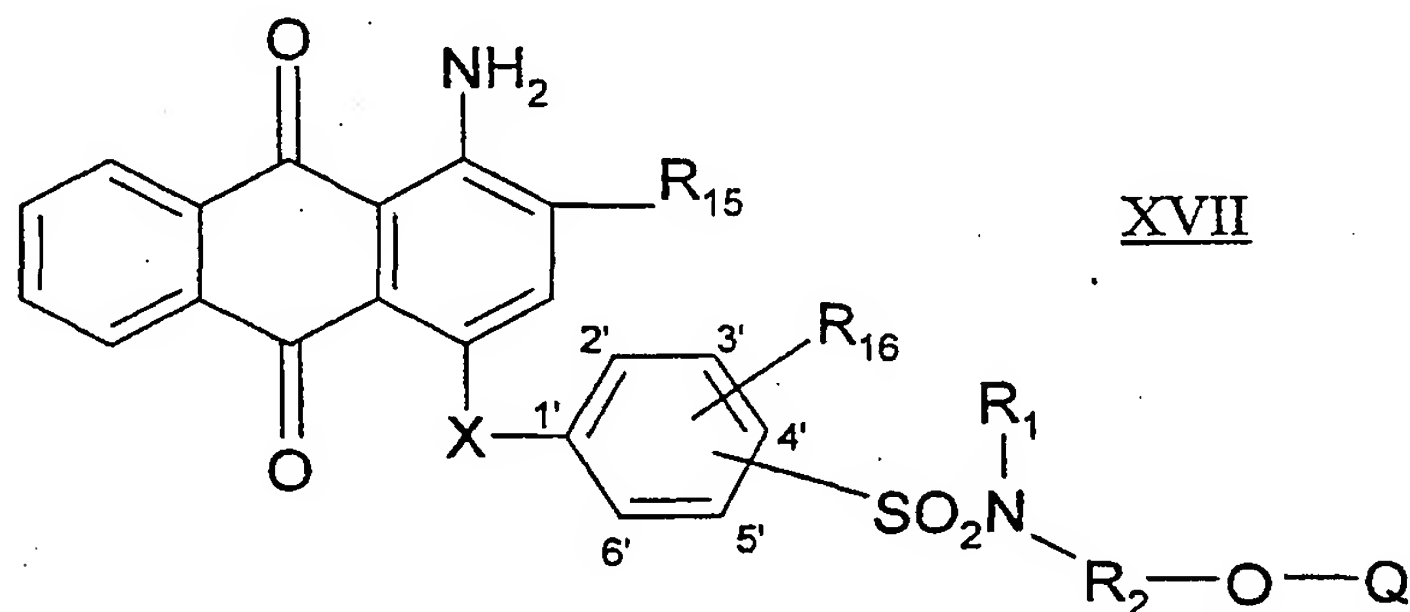


- R_{16} is hydrogen or 1-2 groups selected from C_1 - C_6 -alkyl, C_1 - C_6 -alkoxy and halogen;

X is $-O-$, $-S-$, $-SO_2-$, or $-O-C_2-C_6$ alkylene; and

Q is $-COC(R_3)=CH_2$ wherein R_3 is selected from hydrogen or methyl.

9. A photopolymerizable colorant according to Claim 1 having the formula



wherein

R_1 is selected from hydrogen, C_1 - C_6 alkyl, and $-R_2-OQ$;

- R_2 is selected from C_2 - C_8 alkylene, arylene, C_3 - C_8 cycloalkylene, arylene - C_1 - C_6 alkylene, arylene-oxy- C_1 - C_6 alkylene, arylene-thio - C_1 - C_6 alkylene, 1,4-cyclohexylenedimethylene and $-(-CH_2CH_2O)_m-CH_2CH_2-$;

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m is 1-3;

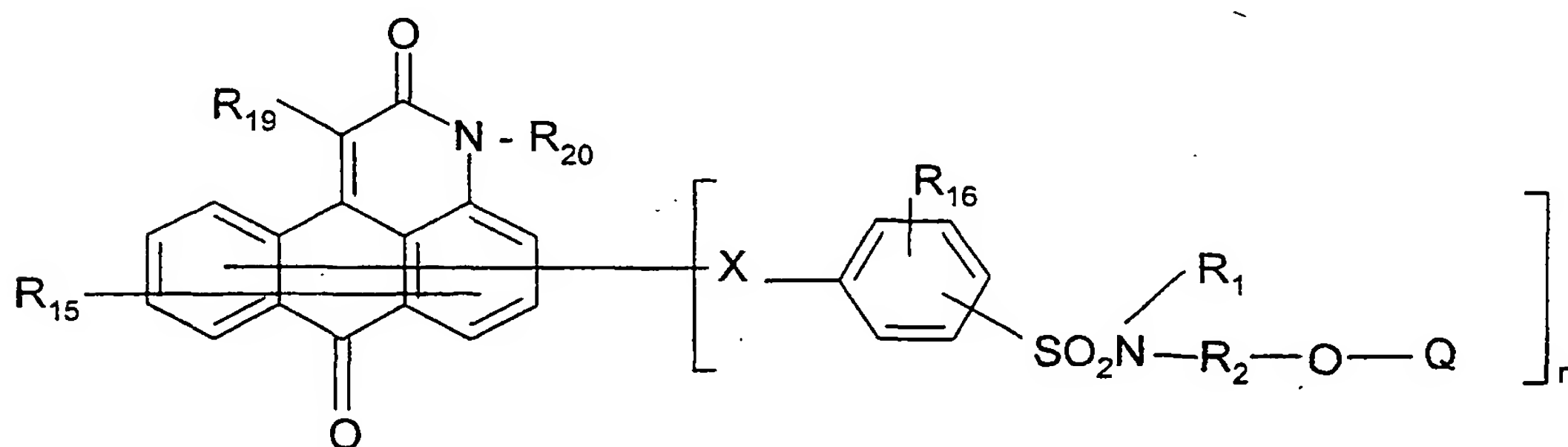
R₁₅ is selected from hydrogen, C₁-C₆-alkoxy; -OCH₂CH₂(O CH₂CH₂)₁₋₃OR', wherein R' is selected from hydrogen, C₁-C₆-alkyl and C₂-C₆-alkanoyloxy; halogen; hydroxy; C₁-C₆-alkylthio; arylthio; aryl; aryloxy; arylsulfonyl; C₂-C₆-alkanoyl; aroyl; C₂-C₆-alkanoyloxy; C₂-C₆-alkoxycarbonyl; heteroaryl; heteroarylthio; cyano; nitro; trifluoromethyl; thiocyno; -SO₂C₁-C₆-alkyl; -SO₂NH₂; -SO₂NHC₁-C₆-alkyl; -SO₂N(C₁-C₆ alkyl)₂; -SO₂N(C₁-C₆ alkyl)aryl; -SO₂NH-aryl; -CONH₂; -CONHC₁-C₆-alkyl; -CON(C₁-C₆-alkyl)₂; -CONH-aryl; and -CON(C₁-C₆alkyl) aryl;

R₁₆ is hydrogen or 1-2 groups selected from C₁-C₆-alkyl, C₁-C₆-alkoxy and halogen;

X is -NH- or -S-; and

Q is -COC(R₃)=CH₂ wherein R₃ is selected from hydrogen or methyl.

10. A photopolymerizable colorant according to Claim 1 having the formula



wherein

R₁ is selected from hydrogen, C₁ - C₆ alkyl, substituted C₁ - C₆ alkyl, C₃ - C₈ cycloalkyl, aryl and -R₂-OQ;

R₂ is selected from C₂ - C₈ alkylene, arylene, C₃ - C₈ cycloalkylene, arylene - C₁ - C₆ alkylene, arylene-oxy-C₁ - C₆ alkylene, arylene-thio - C₁ - C₆ alkylene, 1,4-cyclohexylenedimethylene and -(-CH₂CH₂O)_m-CH₂CH₂-;

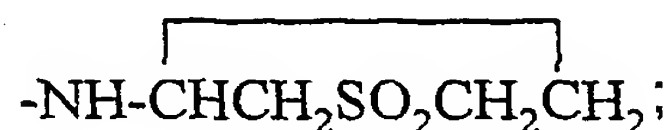
m is 1-3;

n is 1-4;

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R_{15} is hydrogen or R_{15} represents 1-4 groups selected from amino; C_1 - C_8 -alkylamino; C_1 - C_8 -alkylamino substituted with one or more groups selected from hydroxy, cyano, halogen, aryl, heteroaryl, C_3 - C_8 -cycloalkyl, furyl, C_1 - C_6 -alkoxy, C_1 - C_6 -alkylthio, arylthio, aryloxy and $-OCH_2CH_2O(OCH_2CH_2)_{1-3}OR'$, wherein R' is
 5 selected from hydrogen, C_1 - C_6 -alkyl and C_2 - C_6 -alkanoyloxy; C_3 - C_8 -cycloalkyl-amino; C_3 - C_8 -alkenylamino; C_3 - C_8 -alkynylamino; arylamino; furfurylamino; C_1 - C_6 -alkoxy; $-OCH_2CH_2(OCH_2CH_2)_{1-3}OR'$, wherein R' is as previously defined; halogen; hydroxy; C_1 - C_6 -alkylthio; arylthio; aryl; aryloxy; arylsulfonyl; C_2 - C_6 -alkanoyl; aroyl; C_2 - C_6 -alkanoyloxy; C_2 - C_6 -alkoxycarbonyl; heteroaryl;
 10 heteroarylthio; cyano; nitro; trifluoromethyl; thiocyano; $-SO_2C_1$ - C_6 -alkyl; $-SO_2NH_2$; $-SO_2NHC_1$ - C_6 -alkyl; $-SO_2N(C_1$ - C_6 alkyl) $_2$; $-SO_2N(C_1$ - C_6 alkyl)aryl; $-SO_2NH$ -aryl; $-CONH_2$; $-CONHC_1$ - C_6 -alkyl; $-CON(C_1$ - C_6 -alkyl) $_2$; $-CONH$ -aryl; $-CON(C_1$ - C_6 alkyl) aryl; C_1 - C_6 alkyl; tetrahydrofurfurylamino; $-CH_2$ -cyclohexane-1,4-diyl- CH_2OR' , wherein R' is as previously defined; or

15



R_{16} is hydrogen or 1-2 groups selected from C_1 - C_6 -alkyl, C_1 - C_6 -alkoxy and halogen;

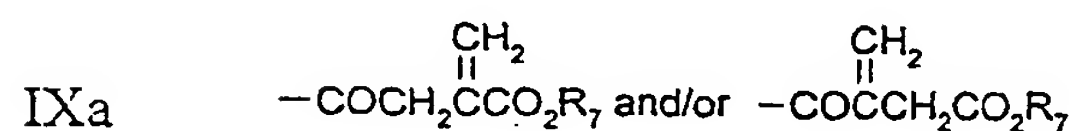
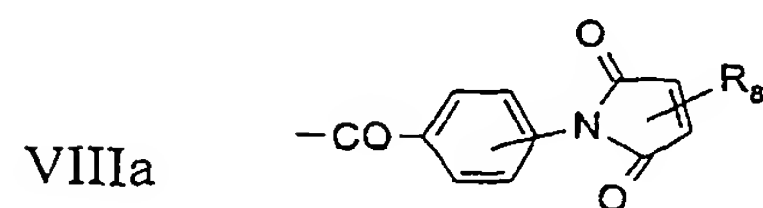
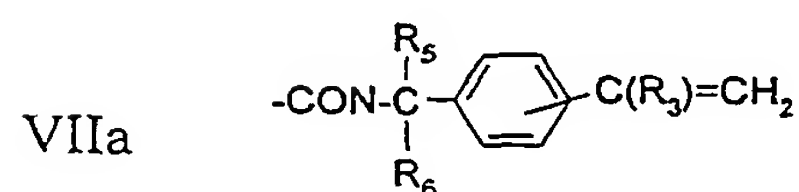
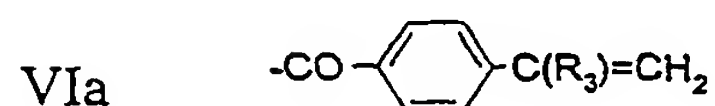
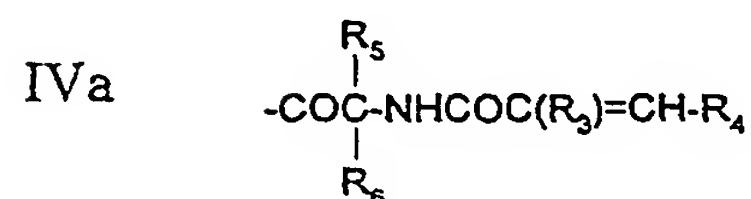
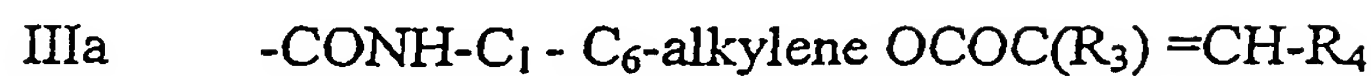
20 R_{19} is selected from hydrogen, cyano, C_1 - C_6 -alkoxy, C_1 - C_6 -alkylthio, aryl, arylamino, aryloxy, arylthio, heteroaryl, heteroarylthio, halogen, C_2 - C_6 -alkoxy-carbonyl, aroyl, C_1 - C_6 -alkylsulfonyl, arylsulfonyl and C_1 - C_6 -alkylamino;

R_{20} is selected from hydrogen, C_1 - C_8 -alkyl, substituted C_1 - C_8 -alkyl as defined above, aryl and C_3 - C_8 -cyloalkyl;

25 X is $-NH-$, $-O-$, $-S-$, $-SO_2-$, or $-O-C_2-C_6$ alkylene; and

Q is an ethylenically-unsaturated, photopolymerizable group selected from the following organic radicals:

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wherein

R_3 is selected from hydrogen or $\text{C}_1 - \text{C}_6$ alkyl;

R_4 is selected from hydrogen, $\text{C}_1 - \text{C}_6$ alkyl;

phenyl; phenyl substituted with one or more groups selected from $\text{C}_1 - \text{C}_6$ alkyl,

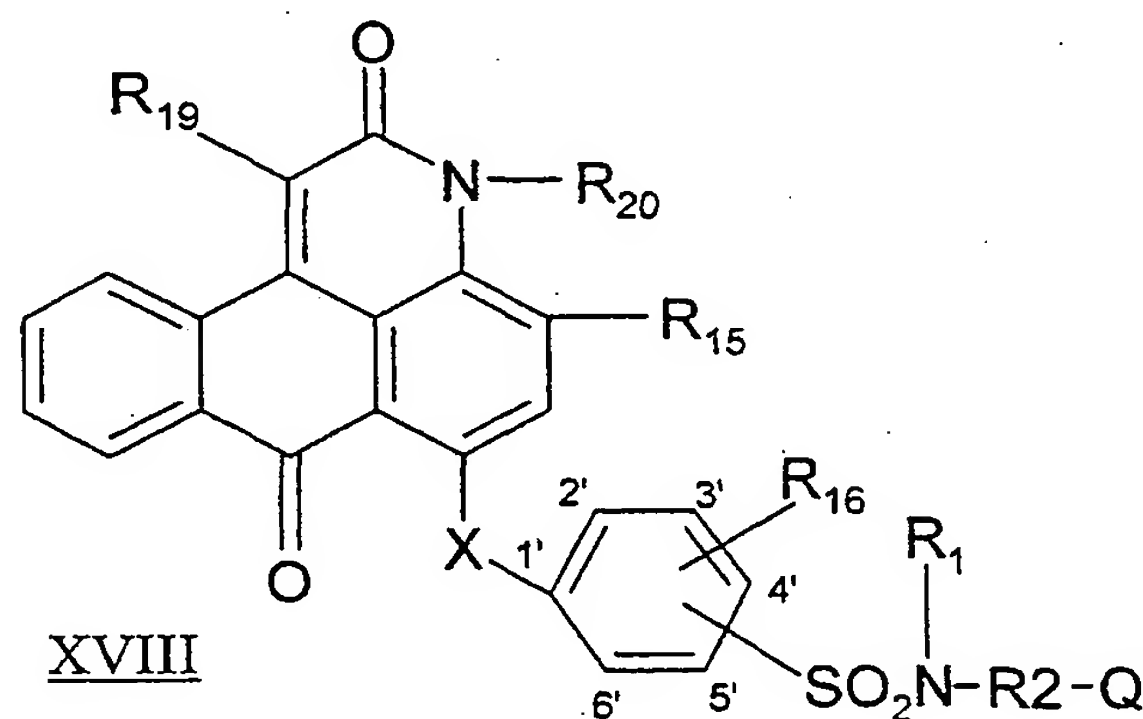
5 $\text{C}_1 - \text{C}_6$ alkoxy, $-\text{N}(\text{C}_1 - \text{C}_6 \text{ alkyl})_2$, nitro, cyano, $\text{C}_2 - \text{C}_6$ alkoxycarbonyl, $\text{C}_2 - \text{C}_6$ alkanoyloxy and halogen; 1- and 2-naphthyl; 1- and 2-naphthyl substituted with $\text{C}_1 - \text{C}_6$ alkyl and $\text{C}_1 - \text{C}_6$ alkoxy; 2- and 3-thienyl; 2- and 3-thienyl substituted with $\text{C}_1 - \text{C}_6$ alkyl or halogen; 2- and 3-furyl; 2- and 3-furyl substituted with $\text{C}_1 - \text{C}_6$ alkyl;

10 R_5 and R_6 are independently selected from hydrogen, $\text{C}_1 - \text{C}_6$ alkyl, substituted $\text{C}_1 - \text{C}_6$ alkyl, aryl or may be combined to represent a $-(\text{CH}_2)-_{3-5}$ radical;

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R_7 is hydrogen or a group selected from $C_1 - C_6$ alkyl, substituted $C_1 - C_6$ alkyl, $C_3 - C_8$ alkenyl, $C_3 - C_8$ cycloalkyl and aryl; and
 R_8 is selected from hydrogen, $C_1 - C_6$ alkyl and aryl.

- 5 11. A photopolymerizable colorant according to Claim 1 having the formula



wherein

R_1 is selected from hydrogen, $C_1 - C_6$ alkyl, and $-R_2-OQ$;

R_2 is selected from $C_2 - C_8$ alkylene, arylene, $C_3 - C_8$ cycloalkylene, arylene- $C_1 - C_6$ alkylene, arylene-oxy- $C_1 - C_6$ alkylene, arylene-thio- $C_1 - C_6$ alkylene, 1,4-cyclohexylenedimethylene and $-(-CH_2CH_2O)_m-CH_2CH_2-$;

m is 1-3;

R_{15} is hydrogen, C_1-C_6 -alkyl, C_1-C_6 -alkoxy, or halogen;

R_{16} is hydrogen, C_1-C_6 -alkyl, C_1-C_6 -alkoxy and halogen;

R_{19} is selected from hydrogen, cyano, C_1-C_6 -alkoxy, C_1-C_6 -alkylthio, aryl, arylamino, aryloxy, arylthio, heteroaryl, heteroarylthio, halogen, C_2-C_6 -alkoxy-carbonyl, aroyl, C_1-C_6 -alkylsulfonyl, arylsulfonyl and C_1-C_6 -alkylamino;

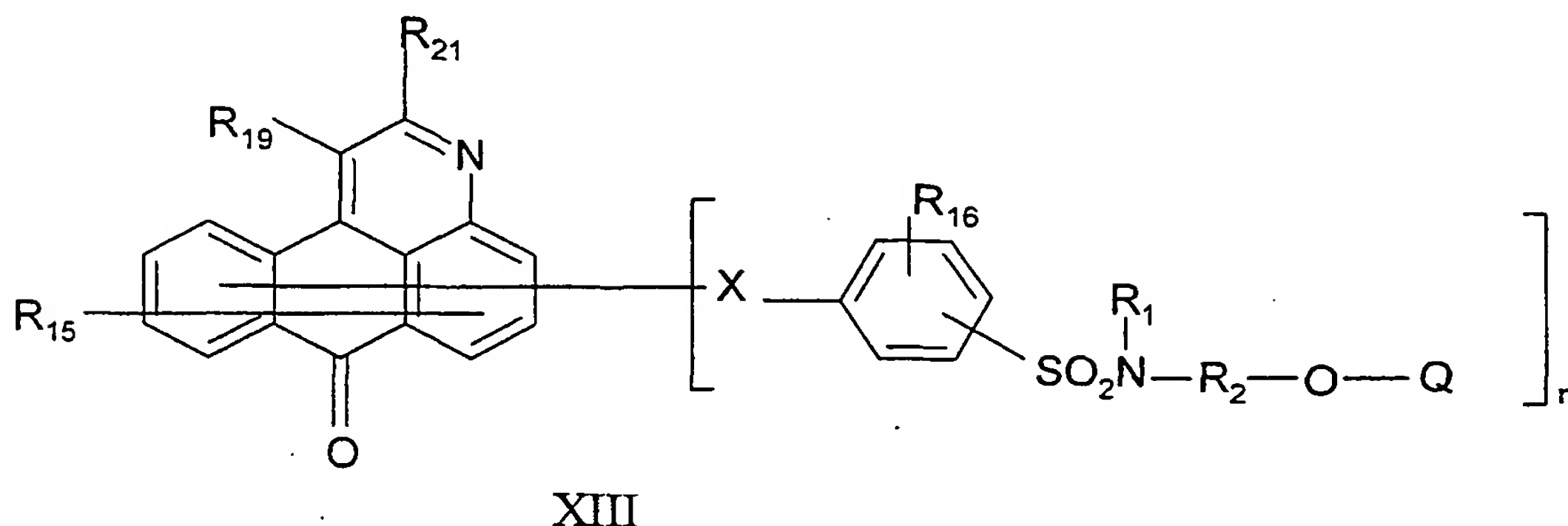
R_{20} is selected from C_1-C_8 -alkyl and substituted C_1-C_8 -alkyl as defined above;

X is $-NH-$ or $-S-$; and

Q is $-COC(R_3)=CH_2$ wherein R_3 is selected from hydrogen or methyl.

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12. A photopolymerizable colorant according to Claim 1 having the formula



wherein

R_1 is selected from hydrogen, $C_1 - C_6$ alkyl, substituted $C_1 - C_6$ alkyl, $C_3 - C_8$ cycloalkyl, aryl and $-R_2-OQ$;

- 5 R_2 is selected from $C_2 - C_8$ alkylene, arylene, $C_3 - C_8$ cycloalkylene, arylene- $C_1 - C_6$ alkylene, arylene-oxy- $C_1 - C_6$ alkylene, arylene-thio- $C_1 - C_6$ alkylene, 1,4-cyclohexylenedimethylene and $-(CH_2CH_2O)_m-CH_2CH_2-$;

m is 1-3;

n is 1-4;

- 10 R_{15} is hydrogen or R_{15} represents 1-4 groups selected from amino; C_1-C_8 -alkylamino; C_1-C_8 -alkylamino substituted with one or more groups selected from hydroxy, cyano, halogen, aryl, heteroaryl, C_3-C_8 -cycloalkyl, furyl, C_1-C_6 -alkoxy, C_1-C_6 -alkylthio, arylthio, aryloxy and $-OCH_2CH_2O(OCH_2CH_2)_{1-3}OR'$, wherein R' is selected from hydrogen, C_1-C_6 -alkyl and C_2-C_6 -alkanoyloxy; C_3-C_8 -cycloalkyl-amino; C_3-C_8 -alkenylamino; C_3-C_8 -alkynylamino; arylamino; furfurylamino; C_1-C_6 -alkoxy; $-OCH_2CH_2(OCH_2CH_2)_{1-3}OR'$, wherein R' is as previously defined; halogen; hydroxy; C_1-C_6 -alkylthio; arylthio; aryl; aryloxy; arylsulfonyl; C_2-C_6 -alkanoyl; aroyl; C_2-C_6 -alkanoyloxy; C_2-C_6 -alkoxycarbonyl; heteroaryl; heteroarylthio; cyano; nitro; trifluoromethyl; thiocyno; $-SO_2C_1-C_6$ -alkyl;
- 15 $-SO_2NH_2$; $-SO_2NHC_1-C_6$ -alkyl; $-SO_2N(C_1-C_6\text{ alkyl})_2$; $-SO_2N(C_1-C_6\text{ alkyl})\text{aryl}$;
- 20 $-SO_2NH\text{-aryl}$; $-CONH_2$; $-CONHC_1-C_6$ -alkyl; $-CON(C_1-C_6\text{ alkyl})_2$; $-CONH\text{-aryl}$;

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-CON(C₁-C₆alkyl) aryl; C₁-C₆ alkyl; tetrahydrofurfurylamino; -CH₂-cyclohexane-1,4-diyl-CH₂OR', wherein R' is as previously defined; or

R₁₆ is hydrogen or 1-2 groups selected from C₁-C₆-alkyl, C₁-C₆-alkoxy and halogen;

5 R₁₉ is selected from hydrogen, cyano, C₁-C₆-alkoxy, C₁-C₆-alkylthio, aryl, arylamino, aryloxy, arylthio, heteroaryl, heteroarylthio, halogen, C₂-C₆-alkoxy-carbonyl, aroyl, C₁-C₆-alkylsulfonyl, arylsulfonyl and C₁-C₆-alkylamino;

10 R₂₁ is selected from hydrogen, C₁-C₆-alkyl, aryl and -N(R₂₂)R₂₃, wherein R₂₂ and R₂₃ independently are selected from hydrogen, C₃-C₈-cycloalkyl, C₁-C₆-alkyl and C₁-C₆-alkyl substituted with C₁-C₆-alkoxy, hydroxy, halogen, C₂-C₆-alkanoyloxy, aryl and C₃-C₈-cycloalkyl; or R₂₂ and R₂₃ in combination represent a divalent radical having the formulas (-CH₂)₄₋₆ and -CH₂CH₂-L-CH₂CH₂-, wherein L is a divalent linking group selected from -O-, -S-, -SO₂- and -N(R₂₄), wherein R₂₄ is selected from hydrogen, C₁-C₆-alkyl, aryl, aroyl, C₂-C₆-alkanoyl, C₁-C₆-alkylsulfonyl and arylsulfonyl;

15 X is -NH-, -O-, -S-, -SO₂-, or -O-C₂-C₆ alkylene; and

Q is an ethylenically-unsaturated, photopolymerizable group selected from the following organic radicals:

Ia -COC(R₃)=CH-R₄

IIa -CONHCOC(R₃)=CH-R₄

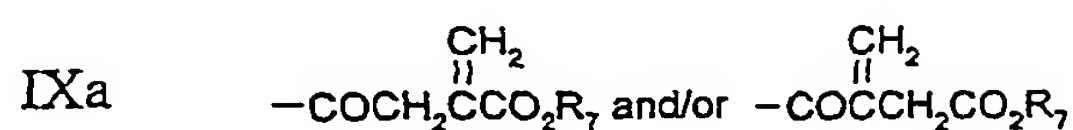
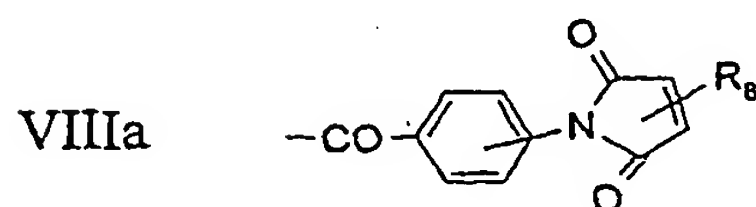
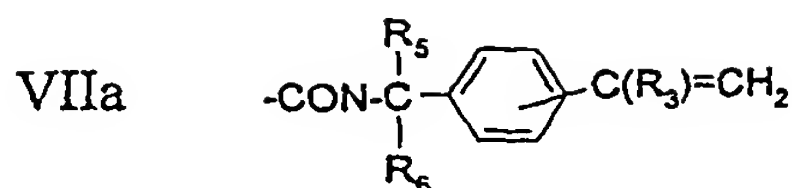
IIIa -CONH-C₁-C₆-alkylene OCOC(R₃)=CH-R₄

IVa
$$\begin{array}{c} \text{R}_5 \\ | \\ \text{-COC-NHCOC(R}_3\text{)=CH-R}_4 \\ | \\ \text{R}_6 \end{array}$$

Va -COCH=CH-CO₂R₇

VIa
$$\text{-CO-} \langle \text{benzene ring} \rangle \text{-C(R}_3\text{)=CH}_2$$

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wherein

R_3 is selected from hydrogen or $C_1 - C_6$ alkyl;

R_4 is selected from hydrogen, $C_1 - C_6$ alkyl;

phenyl; phenyl substituted with one or more groups selected from $C_1 - C_6$ alkyl,

- 5 $C_1 - C_6$ alkoxy, $-N(C_1 - C_6 \text{ alkyl})_2$, nitro, cyano, $C_2 - C_6$ alkoxycarbonyl, $C_2 - C_6$ alkanoyloxy and halogen; 1- and 2-naphthyl; 1- and 2-naphthyl substituted with $C_1 - C_6$ alkyl and $C_1 - C_6$ alkoxy; 2- and 3-thienyl; 2- and 3-thienyl substituted with $C_1 - C_6$ alkyl or halogen; 2- and 3-furyl; 2- and 3-furyl substituted with $C_1 - C_6$ alkyl;

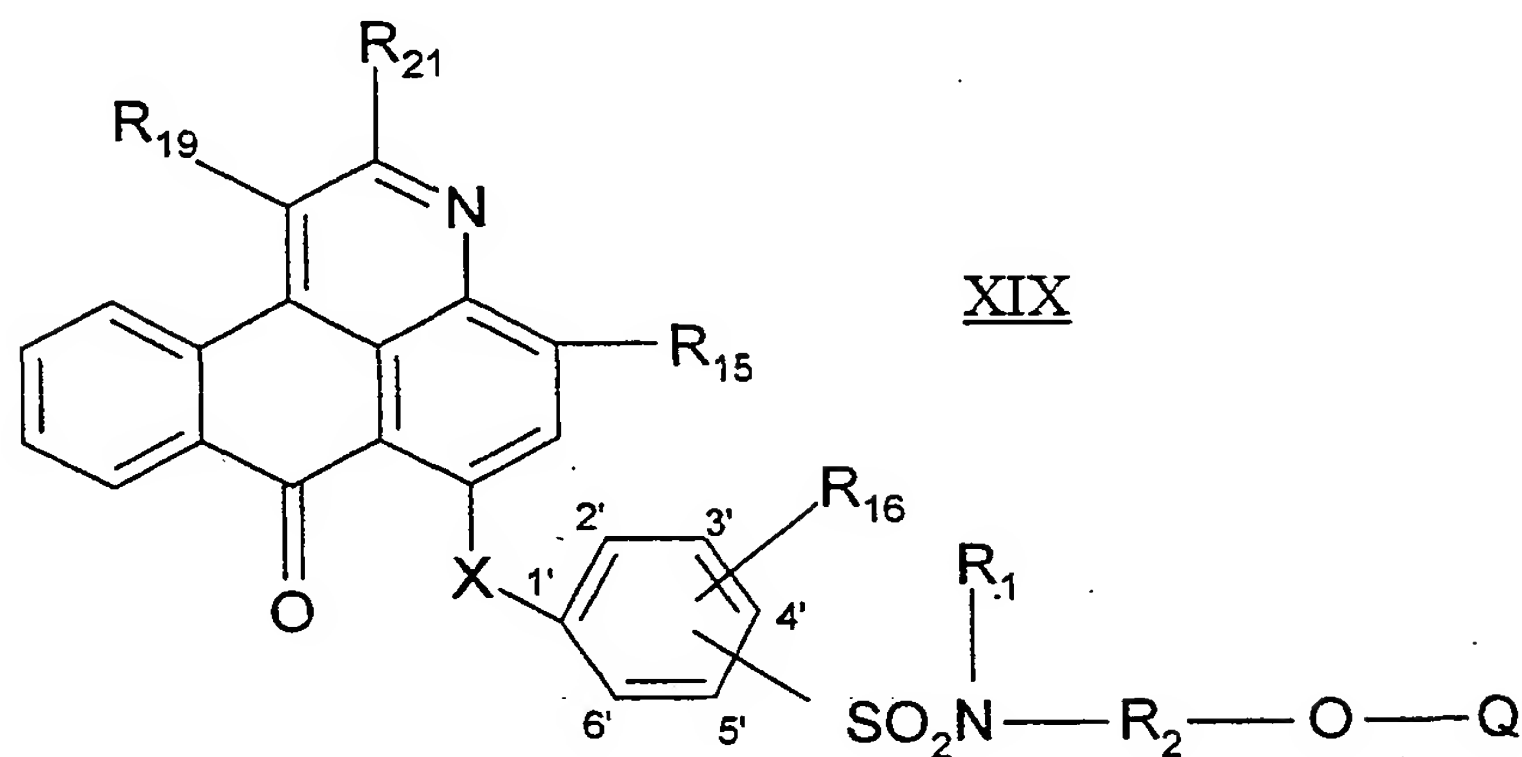
- 10 R_5 and R_6 are independently selected from hydrogen, $C_1 - C_6$ alkyl, substituted $C_1 - C_6$ alkyl, aryl or may be combined to represent a $-(-CH_2-)-_{3-5}$ radical;

R_7 is hydrogen or a group selected from $C_1 - C_6$ alkyl, substituted $C_1 - C_6$ alkyl, $C_3 - C_8$ alkenyl, $C_3 - C_8$ cycloalkyl and aryl; and

- 15 R_8 is selected from hydrogen, $C_1 - C_6$ alkyl and aryl.

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13. A photopolymerizable colorant according to Claim 1 having the formula



wherein

R_1 is selected from hydrogen, $C_1 - C_6$ alkyl, and $-R_2-OQ$;

- R_2 is selected from $C_2 - C_8$ alkylene, arylene, $C_3 - C_8$ cycloalkylene, arylene
 5 - $C_1 - C_6$ alkylene, arylene-oxy- $C_1 - C_6$ alkylene, arylene-thio- $C_1 - C_6$ alkylene,
 1,4-cyclohexylenedimethylene and $-(CH_2CH_2O)_m-CH_2CH_2-$;

m is 1-3;

R_{15} is hydrogen, C_1-C_6 -alkyl or halogen;

- R_{16} is hydrogen or 1-2 groups selected from C_1-C_6 -alkyl, C_1-C_6 -alkoxy and
 10 halogen;

R_{19} is selected from hydrogen and cyano;

- R_{21} is $-N(R_{22})R_{23}$, wherein R_{22} and R_{23} are independently selected from
 C_1-C_6 -alkyl or R_{22} and R_{23} in combination are a divalent radical having the
 formulas $(-CH_2-)_{4-6}$ and $-CH_2CH_2-L-CH_2CH_2-$, wherein L is a divalent linking
 15 group selected from $-O-$, $-S-$, $-SO_2-$ and $-N(R_{24})$, wherein R_{24} is selected from
 hydrogen, C_1-C_6 -alkyl, aryl, aroyl, C_2-C_6 -alkanoyl, C_1-C_6 -alkylsulfonyl and
 arylsulfonyl;

X is $-NH-$ or $-S-$; and

Q is $-COC(R_3)=CH_2$ wherein R_3 is selected from hydrogen or methyl.

- 20 14. A coating composition comprising (i) one or more polymerizable vinyl
 compounds, (ii) one or more of the colorant compounds of Claim 1, and (iii) a
 photoinitiator.

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15. A coating composition according to Claim 14 comprising (i) one or more polymerizable vinyl compounds, (ii) one or more of the colorant compounds of Claim 2 present in a concentration of 0.05 to 15 weight percent based on the weight of component (i), and (iii) a photoinitiator present in a concentration of 1 to 15 weight percent based on the weight of the polymerizable vinyl compound(s) present in the coating composition.

16. A coating composition according to Claim 15 wherein the polymerizable vinyl compounds comprise a solution of a polymeric, polymerizable vinyl compound selected from acrylated and methacrylated polyesters, acrylated and methacrylated polyethers, acrylated and methacrylated epoxy polymers, acrylated or methacrylated urethanes, and mixtures thereof, in a diluent selected from monomeric acrylate and methacrylate esters.

17. A polymeric coating composition comprising a polymer of one or more acrylic acid esters, one or more methacrylic acid esters and/or other copolymerizable vinyl compounds, having copolymerized therein one or more of the colorant compounds defined in Claim 1.

18. A polymeric composition according to Claim 17 comprising a coating of an acrylic polymer of one or more acrylic acid esters, one or more methacrylic acid esters or a mixture thereof having copolymerized therein one or more of the colorant compounds defined in Claim 2.

19. A polymeric composition according to Claim 17 comprising a coating of an unsaturated polyester containing one or more maleate/fumarate residues; one or more monomers which contain one or more vinyl ether groups, one or more vinyl ester groups, or a combination thereof, and, optionally, one or more acrylic or

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methacrylic acid esters; or a mixture thereof having copolymerized therein one or more of the colorant compounds defined in Claim 2.

20. A polymeric coating according to Claim 18 containing from 0.05 to 15.0
5 weight percent of the residue of one or more of the dye compounds of Claim 2 based on the weight of the coating.

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
14 February 2002 (14.02.2002)

PCT

(10) International Publication Number
WO 02/12403 A3

(51) International Patent Classification⁷: **C09B 69/10**,
C09D 133/04, C08F 220/38, 290/14

231 Saddle Ridge Road, Kingsport, TN 37664 (US). **DE WIT, Jos, Simon**; 205 Shoals Road, Kingsport, TN 37663 (US). **JOHNSON, Larry, Keith**; 126 Kingfisher Court, Kingsport, TN 37663 (US).

(21) International Application Number: PCT/US01/24640

(22) International Filing Date: 6 August 2001 (06.08.2001)

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(25) Filing Language: English

(81) Designated States (*national*): CA, JP, MX.

(26) Publication Language: English

(84) Designated States (*regional*): European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR).

(30) Priority Data:
60/223,520 7 August 2000 (07.08.2000) US
09/920,151 1 August 2001 (01.08.2001) US

Published:

- with international search report
- before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments

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(88) Date of publication of the international search report:
11 April 2002

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

WO 02/12403 A3

(54) Title: COLORANTS CONTAINING COPOLYMERIZABLE VINYL GROUPS AND SULFONAMIDE LINKAGES

(57) Abstract: Disclosed are thermally-stable, colored, photopolymerizable compounds containing a vinyl group which are capable of being copolymerized with reactive vinyl monomers to produce colored compositions such as polyacrylates, polymethacrylates, polystyrene, etc. The compounds exhibit good thermal stability, fastness (stability) to UV-light, good solubility in the reactive monomers and good color strength.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 01/24640

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C09B69/10 C09D133/04 C08F220/38 C08F290/14

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C09B C08L C08F C09D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GB 1 235 289 A (IMPERIAL CHEMICAL INDUSTRIES LIMITED) 9 June 1971 (1971-06-09) example 21	1,2
A	ASQUITH R S ET AL: "SELF-COLOURED POLYMERS BASED ON ANTHRAQUINONE RESIDUES" JOURNAL OF THE SOCIETY OF DYERS AND COLOURISTS, SOCIETY OF DYERS AND COLOURISTS. BRADFORD, GB, vol. 93, no. 4, 1 April 1977 (1977-04-01), pages 114-125, XP002033756 ISSN: 0037-9859 cited in the application page 115, left-hand column, paragraph 4 -page 117, right-hand column, paragraph 1 -/--	1-20



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

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- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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- *&* document member of the same patent family

Date of the actual completion of the international search

11 February 2002

Date of mailing of the international search report

20/02/2002

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INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 01/24640

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	GB 1 046 751 A (ASAHI CHEMICAL IND) 26 October 1966 (1966-10-26) claims; examples ---	1-20
A	US 3 364 186 A (ERNST PENNING ET AL) 16 January 1968 (1968-01-16) claims; example 19 ---	1-20
A	EP 0 396 376 A (BAUSCH & LOMB) 7 November 1990 (1990-11-07) claims 1-4; examples 1A-1H & US 5 055 602 A 8 October 1991 (1991-10-08) cited in the application -----	1-20

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 01/24640

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
GB 1235289	A	09-06-1971	NONE	
GB 1046751	A	26-10-1966	NONE	
US 3364186	A	16-01-1968	BE 604017 A	
			CH 415057 B	15-06-1966
			CH 403706 B	31-08-1965
			CH 697362 B	
			CH 762262 A	
			DE 1115926 B	
			DE 1136302 B	
			DE 1141614 B	
			DE 1145136 B	
			DE 1154629 B	
			FR 1295638 A	08-06-1962
			FR 1301002 A	10-08-1962
			FR 1318897 A	22-02-1963
			GB 949404 A	12-02-1964
			GB 914354 A	02-01-1963
			GB 947463 A	
			NL 126420 C	
			NL 133148 C	
			NL 264863 A	
			NL 266982 A	
			NL 281314 A	
			NL 281315 A	
			US 3232691 A	01-02-1966
EP 0396376	A	07-11-1990	US 5055602 A	08-10-1991
			AU 627873 B2	03-09-1992
			AU 5460690 A	08-11-1990
			BR 9002044 A	13-08-1991
			CA 2015636 A1	02-11-1990
			DE 69015426 D1	09-02-1995
			DE 69015426 T2	07-09-1995
			EP 0396376 A1	07-11-1990
			ES 2069007 T3	01-05-1995
			HK 143795 A	15-09-1995
			JP 2788534 B2	20-08-1998
			JP 3072576 A	27-03-1991
			KR 9601744 B1	05-02-1996
			BR 9003752 A	12-11-1991
			US 4997897 A	05-03-1991